

X-ray absorption fine structure spectroscopic study of uranium nitrides

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Abstract Uranium mononitride (UN), sesquinitride (U_2N_3) and dinitride (UN_2) were characterized by extended X-Ray absorption fine structure spectroscopy. Analysis on UN indicate the presence of three uranium shells at distances of 3.46(3), 4.89(5) and 6.01(6) Å and a nitrogen shell at a distance of 2.46(2) Å. For U_2N_3 , two absorbing uranium atoms at different crystallographic positions are present in the structure. One of the uranium atoms is surrounded by nitrogen atoms at 2.28(2) Å and by uranium atoms at 3.66(4) and 3.95(4) Å. The second type of uranium atom is surrounded by nitrogen atoms at 2.33(2) and 2.64(3) Å and by uranium atoms at 3.66(4), 3.95(4) and 5.31(5) Å. Results on UN_2 indicate two uranium shells at 3.71(4) and 5.32(5) Å and two nitrogen shells at 2.28(2)

and 4.34(4) Å. The lattice parameters of UN, U_2N_3 and UN_2 unit cells were respectively determined to be 4.89(5), 10.62(10) and 5.32(5) Å. Those results are well in agreement with those obtained by X-Ray diffraction analysis.

Keywords EXAFS · Uranium · Nitrides · Nuclear fuel

Introduction

Nitride fuels are a proposed fuel matrix for a number of advanced reactor designs and are an attractive option for transmutation of plutonium and other minor actinides in advanced reactors. Nitrides are considered as potential fuels because they have high solid phase solubility for early actinides and excellent thermal and mechanical characteristics. Among ceramic nuclear fuel matrices, nitrides have the highest metal density, and melting point. The metal fraction of nitride fuel matrices is only slightly lower than that of carbide fuel matrices. Thermal conductivity is slightly lower than carbides but significantly higher than oxides. Incorporation of actinides in zirconium nitride matrix has already been proposed for preparation of transmutation targets. In this context, the local structure of uranium in ZrN has been characterized by extended X-Ray absorption fine structure spectroscopy (EXAFS) spectroscopy [1]. Uranium dinitride ($U^{VI}N_2$), mononitride ($U^{III}N$) and sesquinitride ($U_2^{III/VI}N_3$) are the common nitrides of this system. Uranium mononitride and dinitride are indexed in the cubic 3mFm space group, while U_2N_3 in the cubic body centered space group 3Ia [2]. Because of their interest in nuclear applications, these compounds have been studied intensively and characterized by many techniques such as X-ray powder diffraction (XRD), neutron powder diffraction, nuclear magnetic resonance, transmission electron

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microscopy and X-Ray photoelectron spectroscopy [3–6]. EXAFS has proved effective among techniques used for structural characterization in materials. EXAFS has been used to determine the effect of oxygen stoichiometry on structure in uranium oxides and to study the formation of solid solution in (U, Ce) O₂, (Th, U) O₂, (Th, Pu) O₂ [7–9]. Very few XAFS characterization has been done on uranium nitrides. Considering the interest in uranium nitrides for nuclear applications, conducting an EXAFS study is important in developing a more complete body of knowledge on these materials. In the present work, the local structure of uranium in uranium mononitride (UN), sesquinitride (U₂N₃) and dinitride (UN₂) was investigated by XAFS spectroscopy and the structural parameters compared with those obtained by diffraction techniques.

Experimental part

Synthesis

Uranium dioxide was purchased from International Bio-Analytical Industries, Inc. (Boca Raton, Florida) and was used as received. Ammonium bifluoride (reagent grade) was purchased from Fischer Scientific and used as received. Ammonia (experimental grade) and argon gas (ultra-high-purity, 99.9999%) used for synthesis were purchased from Praxair.

UN₂. Uranium dioxide (10.4 g) and ammonium bifluoride (9.2 g) were ground in a mechanical ball mill for 20 min. The resulting product was bottled and left undisturbed for 55 days, at which point the product was confirmed by XRD as (NH₄)₄UF₈. A charge of 200 mg (NH₄)₄UF₈ was loaded in a platinum boat and placed inside a quartz tube. Quartz fittings sealed the tube and allowed gas to be flowed over the sample. After flushing with argon for 10 min, the cover gas was switched to ammonia. The tube furnace reached 800 °C in 30 min, held at temperature for 1 h, and then cooled to room temperature. The powder XRD confirmed the formation of single-phased UN₂. XRD shows the cubic UN₂ lattice parameter to be 5.3050(2) Å, matching that of pure UN₂ and confirming phase purity and corresponding to an exact composition of UN_{1.83} [10].

U₂N₃ (218.7 mg) was synthesized by heating UN₂ (225.4 mg) under an argon atmosphere at 700 °C for 60 min. Purity of the sample was checked by XRD. Initial XRD studies showed this sample to contain U₂N₃ with a lattice parameter of 10.6691(1) Å.

UN. The mononitride was prepared by heating uranium dinitride synthesized as previously described. UN₂ (35.8 mg) was heated at 1,100 °C for 30 min under an argon atmosphere. The resulting product was characterized by XRD and indicated the sample to contain UN (95 wt%)

and UO₂ (5 wt%). The UN cubic lattice parameter was determined to 4.8900(2) Å.

EXAFS measurements

EXAFS measurements were performed at the advanced photon source (APS) at the BESSRC-CAT 12 BM station at Argonne National Laboratory. Samples were prepared by dilution of compounds in boron nitride (0.5–1% mass). XAFS spectra were recorded at the uranium L_{III} edge (17 166 eV), in fluorescence mode at room temperature using a 13 elements germanium detector. A double crystal of Si [1 1 1] was used as a monochromator. Energy calibration was done using a Zr foil (*K* edge = 17 998 eV). For each sample, several EXAFS spectra were recorded in the *k* range [0–14] Å⁻¹ and averaged. The background contribution was removed using Athena [11] software and data analysis performed using WINXAS [12]. For the fitting procedure, amplitude and phase shift function were calculated by FEFF8.2 [13]. The Input files were generated by ATOMS [14] using crystallographic structures of uranium nitrides taken from literature [2]. The adjustments of EXAFS spectra were performed under the constraints $S_0^2 = 0.9$, a single value of energy shift ΔE_0 was used for all scattering. The uncertainty on the coordination number (C.N) is 20%; the uncertainty on the distance (*R*) is 1%.

Results and discussion

UN. The extracted EXAFS spectrum was *k*³-weighted and the Fourier transformation done in the *k*- range [3.5, 12.8] Å⁻¹. The adjusting procedure was conducted using the scattering wave functions determined in UN. The amplitude and path of these scatterings are presented in Supplementary Data (Table S1). A representation UN unit cell is shown in Fig. 1. In the adjusting procedure, the scattering distance of U₀↔U₂, MS₁ and MS₂ were

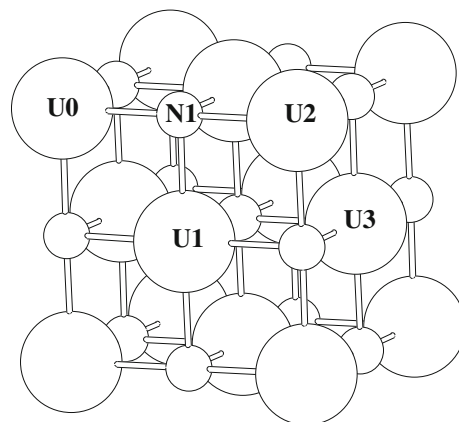


Fig. 1 Unit cell of uranium mononitride (UN)

correlated to a same value; the Debye–Waller factors σ^2 MS₁ and σ^2 MS₂ were correlated to a same value and the degeneracy of these scattering were fixed to the theoretical value; all the other parameters were allowed to vary. The fitted k^3 -EXAFS spectra and Fourier transform are presented in Fig. 2. The structural parameters are presented in Table 1. EXAFS analyses indicate that the environment around the absorbing atom is constituted by nitrogen atoms at 2.46(2) Å and uranium atoms at 3.46(3), 4.89(5) and 6.01(6) Å. Uranium nitride unit cell parameter derived from EXAFS analysis [i.e., 4.89(5) Å] is well in accordance with that determined by XRD refinement [i.e., 4.8900(2) Å]. The ability to distinguish three shells of U atoms and 2 shells of N atoms indicates a highly-structured environment around the absorbing uranium atoms indicate a well-crystallized materials. At distances within the second uranium shell, inter-atomic distances determined by EXAFS are in good agreement with those determined by XRD (Table 2).

A second EXAFS analysis was performed on a nitride sample containing 15 wt% of UO₂ and 85 wt% of UN.

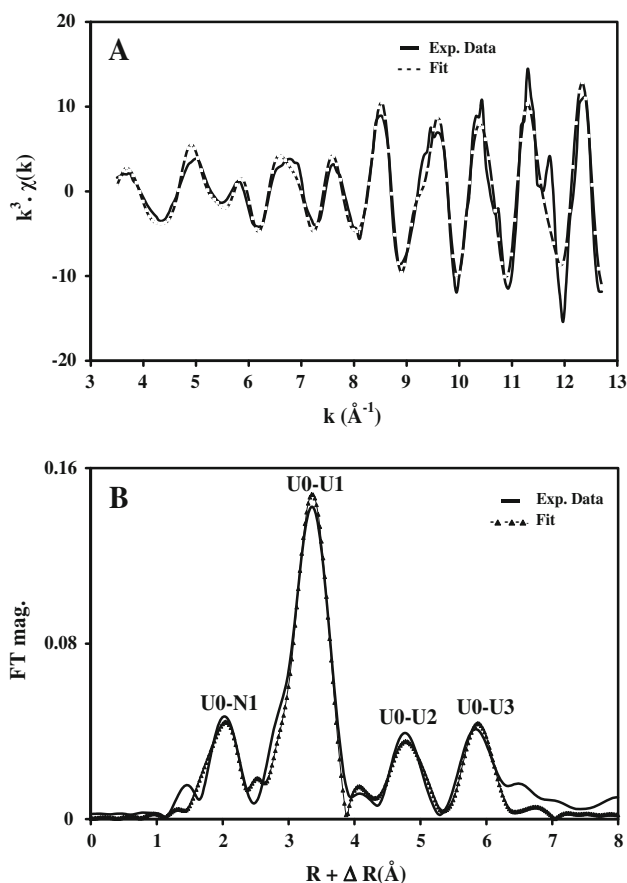


Fig. 2 Fitted experimental k^3 -EXAFS spectra **a** and Fourier transform of k^3 -EXAFS spectra **b** of UN. Adjustment between $k = [3.5, 12.8] \text{ \AA}^{-1}$

Fitted EXAFS parameters are presented in Supplementary Data (Table S2). In this sample, the lattice parameters determined from EXAFS is 4.88(5) Å. The presence of UO₂ in the system does not influence the unit cell of UN enough to be detected by EXAFS analysis. It indicates that UO₂ is not incorporated in UN up to the observed inter-atomic distances, but is present as a separate crystalline phase. Microscopic characterizations that showed the formation of UO₂ as a secondary chemical phase on UN particle surfaces also confirmed this observation [15].

U₂N₃. The extracted EXAFS spectrum was k^3 -weighted and the Fourier transformation done in the k -range [2.5, 11.5] Å⁻¹. The adjusting procedure was conducted using the scattering wave functions determined in U₂N₃. The amplitude and path of these scatterings are presented in Supplementary Data (Table S3). The unit cell of U₂N₃ (Fig. 3) consists of 48 nitrogen atoms and 32 uranium atoms. Eight of these U atoms are in site b (U0B) and the other 24 are in site d (U0A). The U0A and U0B atoms have different local environments and exhibit different EXAFS spectra. Based on the number of U atoms, the EXAFS signal of U0B atoms represents 25% of the total EXAFS spectra of U₂N₃ (U0A represents 75%). The adjustment was performed according to the following procedure:

- The number of uranium atoms around U0A was fixed to 75% of the theoretical value.

Table 1 Structural parameters obtained by adjustment of the k^3 -EXAFS spectra of UN

UN	Structural parameter		
	C.N	R (Å)	σ^2 (Å ²)
U0⇔N1	6	2.46	0.0052
U0⇔U1	11	3.46	0.0027
U0⇔U2	6	4.89	0.0059
MS1	12	4.89	0.0060
MS2	6	4.89	0.0060
U0⇔U3	28	6.01	0.0080
MS3	20	6.92	0.020

Adjustment between $k = [3.5, 12.8] \text{ \AA}^{-1}$

$\Delta E_0 = 6.75 \text{ eV}$

Table 2 Inter-atomic distances (Å) determined by EXAFS and XRD in UN

Distance (Å)	EXAFS	XRD [2]
U0–N1	2.46 (2)	2.440 (5)
U0–U1	3.46 (3)	3.451 (5)
U0–U2	4.89 (5)	4.880 (5)
U0–U3	6.01 (6)	5.977 (5)

- The number of atoms around U0B was fixed to 25% of the theoretical value.

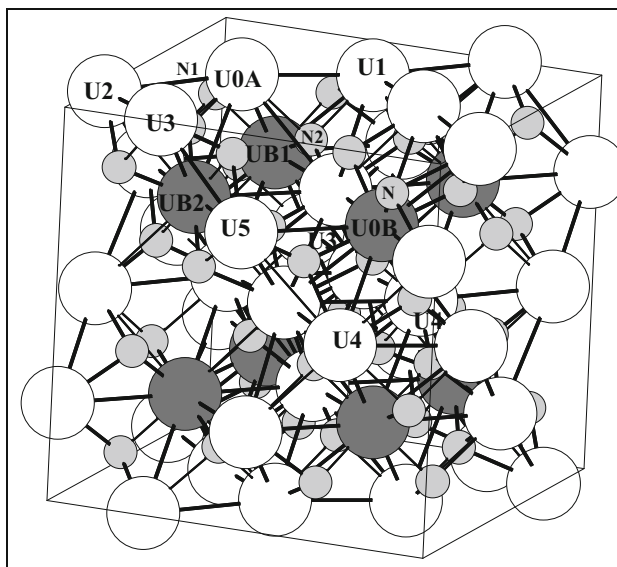


Fig. 3 Unit cell of uranium sesquinitride (U_2N_3)

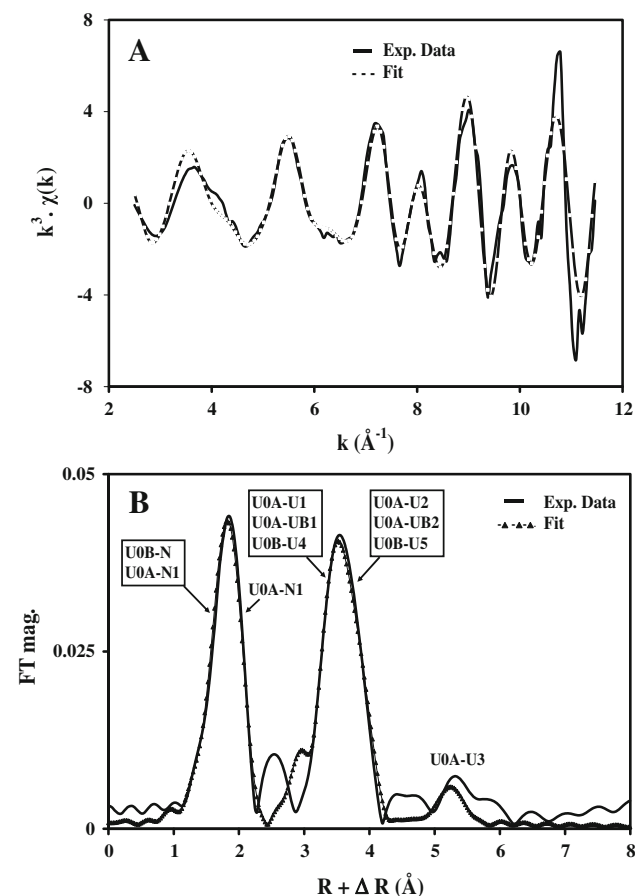


Fig. 4 Fitted experimental k^3 - EXAFS spectra **a** and Fourier transform of k^3 - EXAFS spectra **b** of U_2N_3 . Adjustment between $k = [2.5, 11.5] \text{ \AA}^{-1}$

- The distances U0A–U1, U0A–UB1, U0B–U4 and the corresponding σ^2 were correlated to a same value.
- The distances U0A–U2, U0A–UB2, U0B–U5 and the corresponding σ^2 were correlated to a same value. All the other parameters were allowed to vary.

The fitted k^3 -EXAFS spectra and Fourier transform are presented in Fig. 4. The structural parameters are presented in Table 3. EXAFS analysis indicates that the U0B is surrounded by nitrogen atoms at 2.28(2) Å and by uranium atoms at 3.66(4) and 3.95(4) Å. The environment around U0A is constituted by nitrogen atoms at 2.33(2) and 2.64(3) Å and by uranium atoms at 3.66(4), 3.95(4) and 5.31(5) Å. The unit cell parameter derived from EXAFS analysis is 10.62(10) Å, which is in good agreement with the value determined by powder XRD refinement [i.e., 10.6691(1) Å]. The uranium environment around the absorbing atoms is well in accordance with the literature data (Table 4) while the nitrogen one is slightly different;

Table 3 Structural parameter obtained by adjustment of the k^3 -EXAFS spectra of U_2N_3

U_2N_3	Structural parameter		
	Scattering	C.N	R (Å)
U0A \leftrightarrow N1	3	2.33	0.0048
U0A \leftrightarrow N2	0.5	2.64	0.0086
U0A \leftrightarrow U1	3	3.66	0.0048
U0A \leftrightarrow UB1	1.5	3.66	0.0048
U0A \leftrightarrow U2	3	3.95	0.013
U0A \leftrightarrow UB2	1.5	3.95	0.013
U0A \leftrightarrow U3	3	5.31	0.010
U0B \leftrightarrow N	1.5	2.28	0.0030
U0B \leftrightarrow U4	1.5	3.66	0.0048
U0BU5	1.5	3.95	0.013

Adjustment between $k = [2.5, 11.5] \text{ \AA}^{-1}$

$\Delta E_0 = 8.18 \text{ eV}$

Table 4 Inter-atomic distances (Å) determined by EXAFS and XRD in U_2N_3

Distance (Å)	EXAFS	XRD [2]
U0A–N1	2.33 (2)	2.38 (1)
U0A–N2	2.64 (3)	2.62 (1)
U0A–U1	3.66 (4)	3.65 (1)
U0A–UB1	3.66 (4)	3.65 (1)
U0A–U2	3.95 (4)	3.92 (1)
U0A–UB2	3.95 (4)	3.93 (1)
U0A–U3	5.31 (5)	5.36 (1)
U0B–N	2.28 (2)	2.28 (1)
U0B–U4	3.66 (4)	3.64 (1)
U0B–U5	3.95 (4)	3.96 (1)

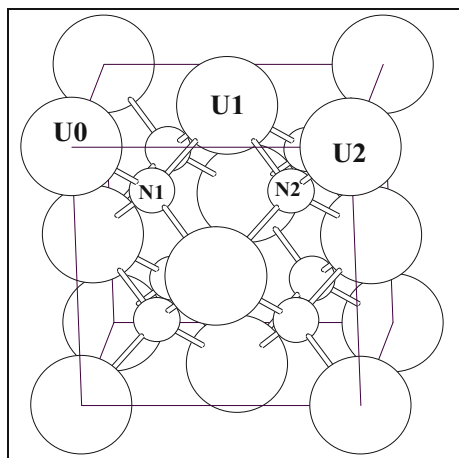


Fig. 5 Unit cell of uranium dinitride (UN_2)

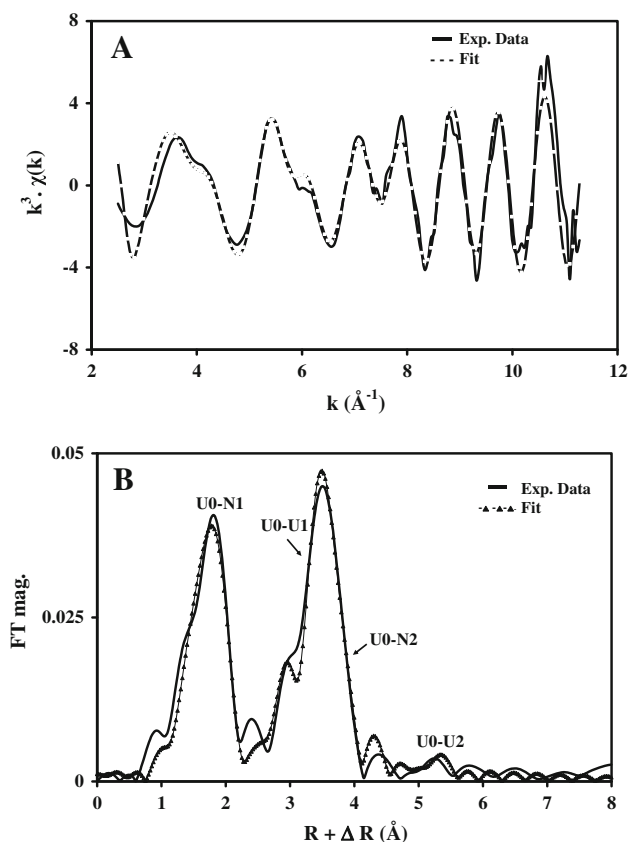


Fig. 6 Fitted experimental k^3 - EXAFS spectra **a** and Fourier transform of k^3 - EXAFS spectra **b** of UN_2 . Adjustment between $k = [2.5, 11.2] \text{ \AA}^{-1}$

the N atoms are more localized around $R \sim 2.33 \text{ \AA}$ which is probably due to the fact that the phase and amplitude corresponding to U0B-N , U0A-N1 and U0A-N2 scattering contribution are nearly superimposed on the Fourier transform.

Table 5 Structural parameter obtained by adjustment of the k^3 -EXAFS spectra of UN_2

UN_2	Structural parameter		
	C.N	$R (\text{ \AA})$	$\sigma^2 (\text{ \AA}^2)$
$\text{U0} \leftrightarrow \text{N1}$	8	2.28	0.012
$\text{U0} \leftrightarrow \text{U1}$	12	3.71	0.0064
$\text{U0} \leftrightarrow \text{N2}$	24	4.34	0.0067
$\text{U0} \leftrightarrow \text{U2}$	6	5.32	0.015

Adjustment between $k = [2.5, 11.2] \text{ \AA}^{-1}$

$\Delta E_0 = 7.27 \text{ eV}$

Table 6 Interatomic distances (\AA) determined by EXAFS and XRD in UN_2

Distance (\AA)	EXAFS	XRD [2]
U0-N1	2.28 (2)	2.29 (5)
U0-U1	3.71 (4)	3.75 (5)
U0-N2	4.34 (4)	4.40 (5)
U0-U2	5.32 (5)	5.31 (5)

UN_2 . The extracted EXAFS spectrum was k^3 -weighted and the Fourier transformation performed in the k - range $[2.5, 11.2] \text{ \AA}^{-1}$. The adjusting procedure was conducted using the scattering wave functions determined in UN_2 . The amplitude and path of these scatterings are presented in Supplementary Data (Table S4). A schematic of UN_2 unit cell is shown in Fig. 5. For the adjustment, the numbers of uranium and nitrogen atoms around U0 were fixed to the theoretical value; all the other parameters were allowed to vary.

The fitted k^3 -EXAFS spectra and Fourier transform are presented in Fig. 6. The structural parameters are presented in Table 5. EXAFS analysis indicate that the environment around the absorbing atom is composed of nitrogen atoms at 2.28(2) and 4.34(4) \AA and uranium atoms at 3.71(4) and 5.32(5) \AA . The lattice parameter of UN_2 derived from EXAFS analysis [i.e., 5.32(5) \AA] is well in agreement with the one determined by XRD powder refinement [i.e., 5.3050(2) \AA]. Inter-atomic distances found by EXAFS are consistent with that of the literature (Table 6).

Conclusions

Uranium nitrides (UN , U_2N_3 , UN_2) were characterized by X-ray absorption fine structure spectroscopy. The very good agreement of the experimental structural parameters with reference values indicates that XAFS spectroscopy is

a suitable technique for the analysis of uranium nitrides. This is particularly important for future studies of localized bonding environments of mixed nitride fuels of uranium containing fission products and higher actinides incorporated into the UN_x matrix. Changes to the local bonding environments within the fuel matrix can be quantified by measuring the EXAFS spectra of Uranium in a matrix containing fission products/actinides in various quantity. Extent of the local matrix distortion can affect the thermal and mechanical properties of the fuel. Study of the EXAFS of un-irradiated materials will provide valuable means to quantify these effects under a wide variety of fuel burnup percentages. In the context of development potential nuclear fuels, plutonium and neptunium nitrides are also considered. Recently, neptunium nitrides were successfully synthesized in our laboratory and characterization of those compounds by XAFS spectroscopy will be subject of further investigation.

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