Experimental report

17/09/2021

Proposal: 6-06-500 **Council:** 4/2020

Title: Assessment of the local structure of U3O7 using neutron total scattering.

Research area: Materials

This proposal is a resubmission of 6-06-494

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Samples: U3O8
U3O7

Instrument	Requested days	Allocated days	From	To
D4	4	4	15/03/2021	19/03/2021

Abstract:

The behavior of nuclear fuel under oxidation and alpha self-irradiation is a key topic for the safety assessment of nuclear (interim) storage facilities. U4O9, U3O7, and U3O8 compounds are part of the series of oxides that form under oxidation. At present, some of these structures are well known, but some discrepancies still exist between the results obtained by diffraction techniques highly sensitive to the long-range order of these structures and methods which probe more the local environment. The structure of U3O7 is defined by the occurence of oxygen cuboctahedra, but the stacking motif determined from neutron diffraction and selected-area electron diffraction experiments is different. One of the possible explanations for the discrepancy is that the former model represents the average of correlated microdomains of nanometric size. Hence, in addition to standard Rietveld refinement of neutron scattering data, PDF (pair distribution functions) analysis should be carried out to gather structural information about the local structure of U3O7.

Assessment of the local structure of U_3O_7 using neutron total scattering

During two days of beamtime at D4 in March, 2021, neutron scattering measurements were performed on polycrystalline powder samples of U_3O_7 and U_3O_8. Because of restrictions following the covid-19 pandemic, the experiments were performed by the local contact and beamline staff without on-site presence of the proposers. The main focus was to collect neutron scattering data up to very high scattering angles (more precisely, high Q ($Å^{-1}$) values) at several temperatures between 1.5 K and room temperature.

The purpose of the experiment was to obtain neutron scattering datasets suitable for performing pair-distribution function (PDF) analysis. In prior experiments (5-21-1119 and EASY-493) the long-range crystalline structure and possible magnetic ordering in several uranium oxides (including U_3O_7 and U_3O_8) was investigated, and significant new insights were obtained [1], or are still being further evaluated. In the case of U_3O_7, the crystal structure is defined by long-range ordering of so-called cuboctahedral oxygen clusters. The refined model still contains residual topological disorder, mainly on the oxygen atoms which constitute the clusters. In the case of U_3O_8 a low-temperature magnetic phase transition has been identified very recently [2]. By performing PDF analysis we aim to evidence additional short-range order signatures which may or may not disagree with the average pictures currently available.

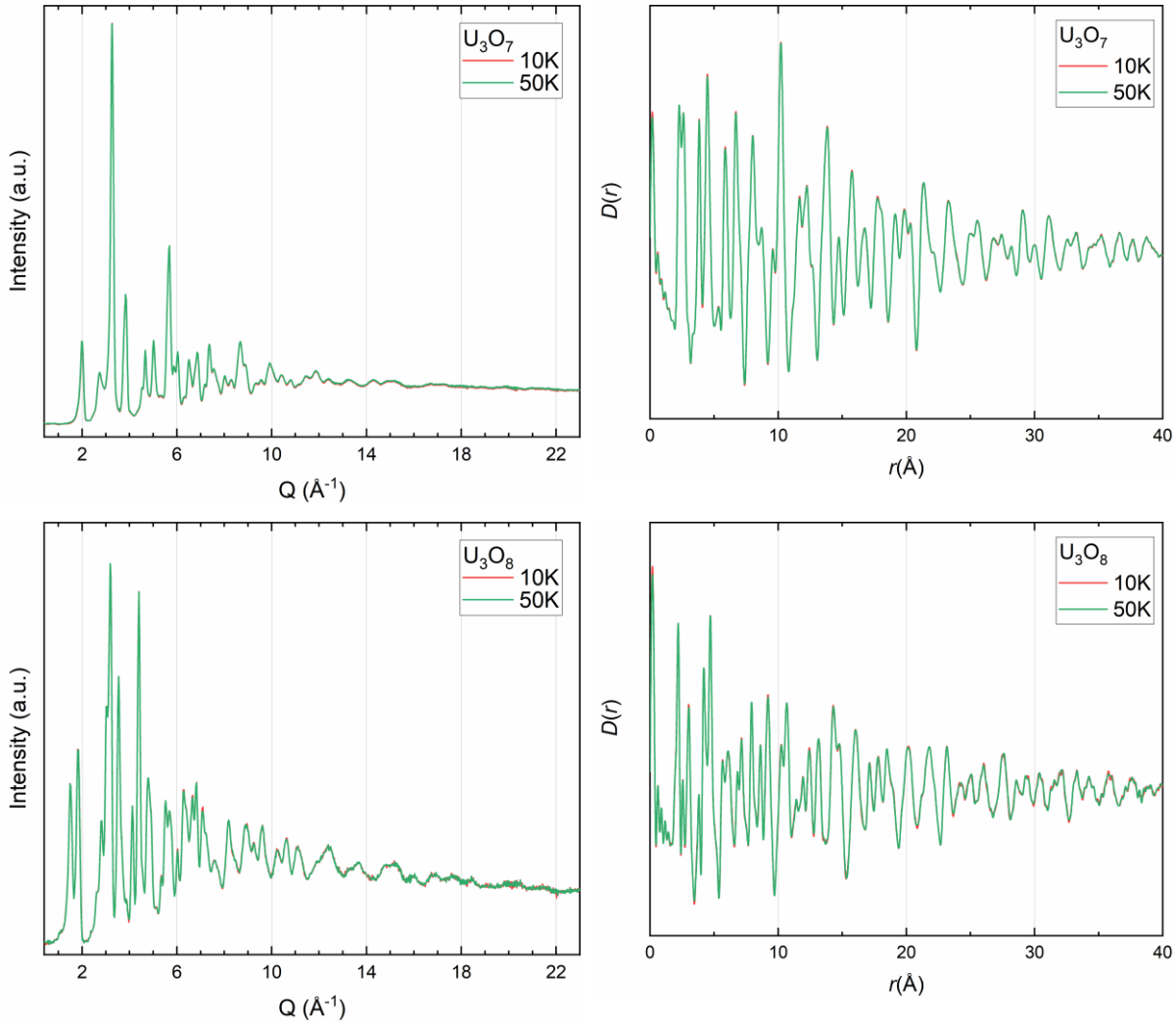

Figure 1. (left) Neutron diffractograms of U_3O_7 and U_3O_8 measured at D4, at 10 K and 50 K. (right) PDF of U_3O_7 and U_3O_8 at 10 K and 50 K derived from the neutron scattering data.

The acquired data was processed by the local contact and deposited for access on the ILL data portal. Data files consist of raw scans, background and subtracted scans, Fourier transforms and derived PDF's for each experimental temperature (6.3 K, 10 K, 20 K, 50K, 100K, 300 K). Data interpretation is ongoing at the moment, and a first qualitative comparison of the scattering data measured at 10 K and 50 K is presented in Figure 1 (top and bottom left). The corresponding PDF's are presented on the right-hand side. At first sight the PDF of U_3O_7 appears quasi identical at both temperatures, in case of U_3O_8, however, some discrepancy is visible at high Q values. A deeper analysis will be carried out in the coming weeks and months.

References

[1] G. Leinders, G. Baldinozzi, C. Ritter, R. Saniz, I. Arts, D. Lamoen, M. Verwerft, Inorganic Chemistry, 60 (2021) 10550.
[2] A. Miskowiec, T. Spano, Z.E. Brubaker, J.L. Niedziela, D.L. Abernathy, R.D. Hunt, S. Finkeldei, Physical Review B, 103 (2021) 205101.