Experimental report

13/02/2020

Proposal: EASY-493 **Council:** 10/2018

Title: Investigating the magnetic ordering at low temperatures in U3O7

Research area: Materials

This proposal is a new proposal

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Experimental team:

Local contacts: Clemens RITTER

Samples: U3O7

Instrument	Requested days	Allocated days	From	To
D20	8	8	30/08/2019	31/08/2019

Abstract:

Uranium(IV) oxide (UO2) exhibits a typical fluorite-type structure. When oxidized, a number of mixed-valence oxide phases are formed which induce a gradual structure modification. The compounds U4O9 [50% U(IV) + 50% U(V)] and U3O7 [33% U(IV) + 67% U(V)] consist of fluorite-derived structures involving long-range ordering of oxygen clusters. The structures of UO2 and U4O9 have been well characterized throughout the years, and very recently our group achieved also significant progress on U3O7. In UO2 an AFM transition occurs around 31K, with a reported magnetic moment of 1.8 μB. In recent investigations performed at ILL (D4) by some of our co-proposers possible short range paramagnetic behaviour at room temperature was found in U4O9. About a decade ago, some colleagues of our institute similarly found magnetic structures in pure pentavalent uranium compounds, e.g. NaUO3 having a magnetic moment of 0.2 μB. We propose to investigate possible magnetic ordering at low temperature in the U3O7 compound to complete the information base on these related compounds. Such knowledge is necessary also in the context of theoretical calculations and modelling work.

Investigating the magnetic ordering at low temperatures in U_3O_7

During two days of beamtime at D2B (wavelength 1.594 Å) in July, 2019, neutron diffraction measurements were performed on five different uranium oxide materials, including U_3O_7. The main focus was to obtain accurate diffraction data at 1.5 K, 50 K, and at room temperature. During the experiments a preliminary assessment of the data was performed, and results were discussed with the local contact (see Figure 1). It became clear that, in order to confidently conclude on the occurrence of magnetic ordering, higher flux diffraction data would be required. Hence, the local contact encouraged us to submit an EASY proposal directed towards the use of beamline D20 (wavelength 2.41 Å) on one particular sample (U_3O_7). The proposal was quickly accepted and the experiment was executed in August, 2019. Diffraction patterns were collected between 0 – 150 °2θ, at temperatures of 100 K and 1.5 K.

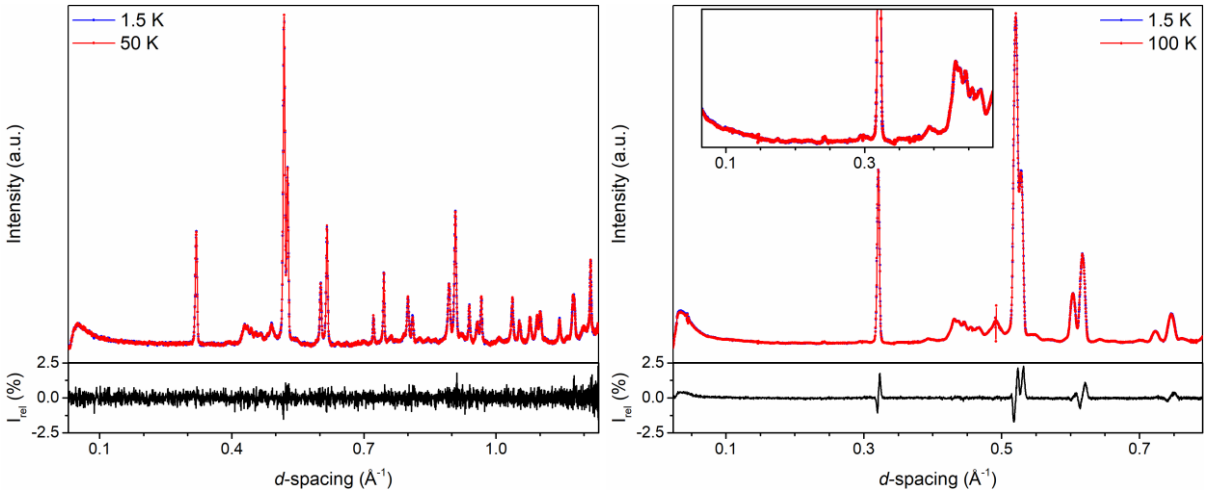

Figure 1. (left) Neutron diffractograms of U_3O_7 measured at D2b (λ = 1.594 Å). A comparison of the data at 50 K and at 1.5 K does not allow to unambiguously conclude on magnetic ordering effects. The data quality is, however, excellent for refining the structure. (right) Neutron diffractograms of U_3O_7 measured at D20 (λ = 2.41 Å). A comparison of the data at 100 K and at 1.5 K is shown, with an inset focusing on the low-angle region. The data quality is such to confidently evaluate magnetic ordering effects, however, no significant difference is observed between the data measured at both temperatures.

The purpose of measuring at 100 K and 1.5 K was to evaluate whether effects of magnetic ordering occur in U_3O_7. In UO_2 an antiferromagnetic transition has been reported to occur at a Néel temperature of 31 K [1,2]. For the higher oxides accurate experimental data on this topic has not yet been reported. Therefore, we decided to probe at the lowest possible temperature (1.5 K) and at a temperature sufficiently above the 31 K limit found in UO_2, i.e. at 100 K. Under both conditions (well below the expected Debye temperature) and if no phase change occurs, the relevant physical properties of the structure in the measured range (e.g. lattice contraction, atomic positions and thermal displacements) will be equivalent, thus allowing an accurate and direct comparison between the two diffraction patterns.

A first qualitative comparison of the both diffraction patterns was performed, after rescaling the intensity of one scan to the maximum of the other scan. Then, a difference profile was calculated and evaluated (see Figure 1). Clearly, the diffraction data obtained at D20 are significantly more intense than the data produced at D2b. The tradeoff is of course a reduction in the spatial resolution and *d*-spacing range available (owing to the higher wavelength used). The data quality proved sufficient to be evaluated

towards signs of magnetic ordering effects, i.e. either the occurrence of additional reflections in the low-angle range, or the change in intensities of main and nuclear superstructure reflections. Based on our analysis it is concluded that no long-range magnetic ordering can be distinguished in U_3O_7.

These results are relevant towards the application of ab-initio calculations to investigate the crystallographic ordering and other properties of the material. The reasoning behind an absence of magnetic ordering in U_3O_7 (unlike in its related structure of UO_2) is not yet final, but some argumentation can be given: (1) U_3O_7 is a mixed-valence (U^{4+} and U^{5+}) compound and it contains different types of local environments, (2) the crystal structure is perturbed by oxygen clusters whose geometries can enhance the competition between electronic correlations and hybridization. The present results will be combined and discussed with the former data obtained at D2b, and will allow us to describe a comprehensive and accurate model of the U_3O_7 crystal structure at temperatures between 1.5 K and room temperature. This work is presently on-going.

References

[1] B.T.M. Willis, R.I. Taylor, Physics Letters, 17 (1965) 188.

[2] J. Faber, G.H. Lander, Phys. Rev. B, 14 (1976) 1151.