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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

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Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Atomic structure of Zr and Mo-alloyed UH3 investigated by x-ray total scattering	**Experiment number**: HC2040
Beamline: ID22	**Date of experiment**: from: Sep 4, 2015 to: Sep 8, 2015	**Date of report**: Nov 7, 2015
Shifts: 12	**Local contact(s)**: Carlotta Giacobbe	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Interaction of hydrogen with uranium is an important issue for its applications in nuclear energy and for understanding magnetism in U and similar (Ce, Pu) systems [1]. Uranium hydrides provide a tool to observe an impact of expansion of the U lattice, allowing formation of U moments and their ferromagnetic ordering. Starting from (bcc) γ-U alloys using doping (Zr, Mo), rapid splat cooling and high-pressure synthesis different varieties of UH_3 were prepared [2,3]. Whereas $(UH_3)_{1-x}Zr_x$ can be obtained in a form of (20 nm) *nanocrystallites with* α-UH_3 *cubic structure*, analogous pure *Mo-alloyed* UH_3 *is almost amorphous* corresponding to very purely (1 nm) nanocrystalline material *with* β-UH_3 *like structure*. Despite of these differences in atomic and micro-structure both types of hydrides behave similarly as ferromagnets with Curie temperature $T_C \approx 170$–200 K. The main reason why 5f magnetism arises (U metal is a weak Pauli paramagnet) can be seen in the U–U spacing. This is enhanced in UH_3 to the proximity of the Hill limit, at which the ordering of U moments can set in due to the 5f band narrowing. A striking phenomena observed in $(UH_3)_{1-x}Zr_x$ by XRD is a large *volume magnetostriction*. Similar abnormalities in temperature dependence of U-spacing are expected in $(UH_3)_{1-x}Mo_x$. In order to get detailed information about *inter-atomic spacing* in UH_3, explore magnetostriction in Mo-alloyed UH_3 and investigate possible size effect, a *pair distribution function* (PDF) study was done in ID22.

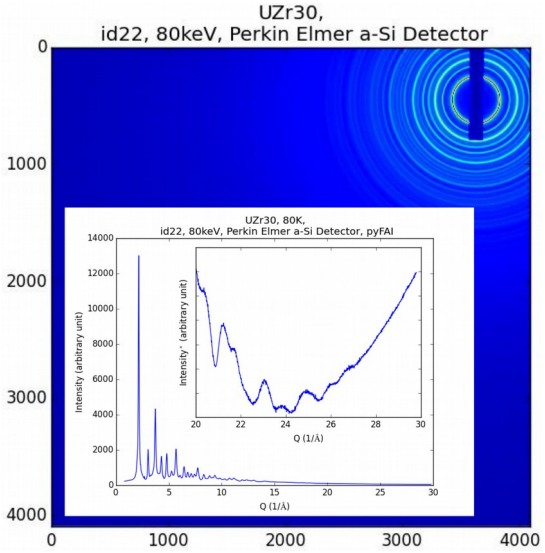

Fig. 1: 2D image data and integrated XRD pattern from $(UH_3)_{0.7}Zr_{0.3}$ sample.

Two sets of Zr and Mo-alloyed samples with 3 dopping levels were prepared. Each sample was mixed with acetone solutable (UHU) glue and encapsulated in a midsection of a polymide (kapton) tube (ID 0.81 mm). The ends of the tube were sealed by Stycast. Experiment was done using x-ray energy 80 keV and additional beam focusing with transfocators. Forward scattering from a spinning capillary in transmission mode was registered by a large 16MPixel Perkin Elmer a-Si Detector. Nitrogen cryostrem was used in temperature range 80–300 K. Azimuthal integration of 2D data was done by `PyFAI` and PDF conversion of XRD patterns by `PDFgetX3`. Thanks to sample transparency for high energy x-rays

and strong scattering from uranium, patterns (Fig. 1) have good statistics (up to $Q_{max} = 2\pi/d \approx 30$ Å^{-1}) and resolution giving an excellent quality PDF (up to $r_{max} >> 40$ Å).

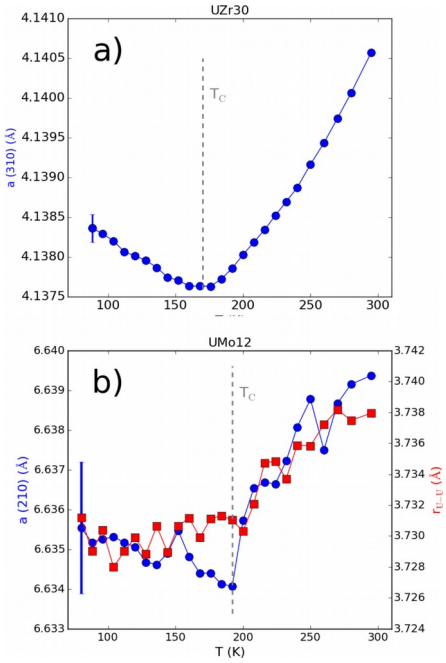

Fig 2.: Temperature dependence of lattice parameters of (a) Zr and (b) Mo-alloyed UH_3 and inter-atomic distance in Mo-(UH_3).

Magnetostriction effect in the temperature dependence of lattice parameter of α-type $(UH_3)_{1-x}Zr_x$ and similar features in inter-atomic distances of β-type Mo-alloyed UH_3 are evident in Fig. 2. Fine details (step-like changes in raw data) of inter-atomic spacing analysis in Mo-UH_3 are nontrivial. Because of very poor crystallinity of hydride it is difficult to *omit instrumental aberrations.* However the effect is always close to T_C and there are correlations with room temperature lattice parameter and Mo-content. Other *arguments are geometrical restrains* onto uranium atoms in the β-UH_3 structure (see later).

Comparison of PDF data of Zr and Mo-alloyed UH_3 demonstrates clearly differences (Fig. 3a) between *α and β-type structures* (Fig. 3b) as well as similarities in the closest U–U spacing giving new insight into the origin of the magnetic ordering. In order to get fine structural details XRD patterns and PDFs were *fitted by a hybrid approach in reciprocal and direct space* using `MSTRUCT` and `DiffPy.xPDFsuite`. Impurities (UO_2 and ZrC) in $(UH_3)_{1-x}Zr_x$ and a situation β-UH_3 is always present in a mixture with α-phase present complications for analysis but already basic fitting gives excellent results (Fig. 4). Fig. 3(b-c) explains the differences between both types of structures. There are 3 possible *different short U–U distances* in β-UH_3 and U atoms form an irregular icosahedron surrounding the central bcc ordered atom. Deviations of a local structure from this model are an objective of ongoing data analysis and an inspiration for ab-initio calculations like in [4].

[1] Shim J. M. *et al.*, Nature 446 (2007) 513. doi: 10.1038/nature05647
[2] Tkach I. *et al.*, Phys. Rev. B 91 (2015) 115116. doi: 10.1103/PhysRevB.91.115116
[3] Havela L. *et al.*, J. Alloys Comp. 645 (2015) S190. doi: 10.1016/j.jallcom.2014.12.258
[4] Starikov S. V. *et al.*, Scripta Mat. 113 (2016) 27. doi: 10.1016/j.scriptamat.2015.10.012

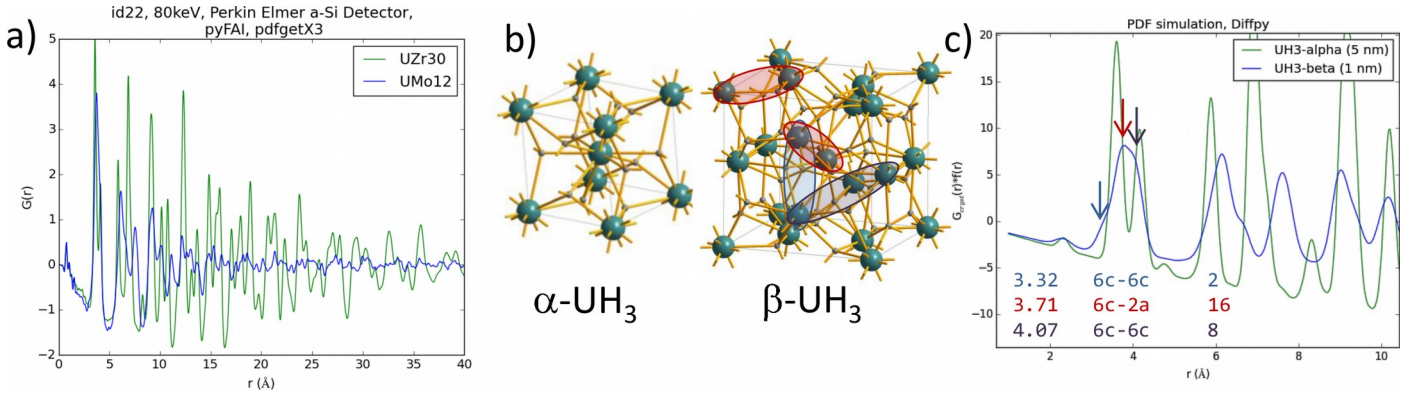

Fig. 3: (a) comparison of experimental PDF of $(UH_3)_{0.70}Zr_{0.30}$ and $(UH_3)_{0.88}Mo_{0.12}$,(b) unit cell structures of α-UH_3 and β-UH_3, (c) `DiffPy` PDF simulations with marked 3 closest U-U distances in β–UH_3.

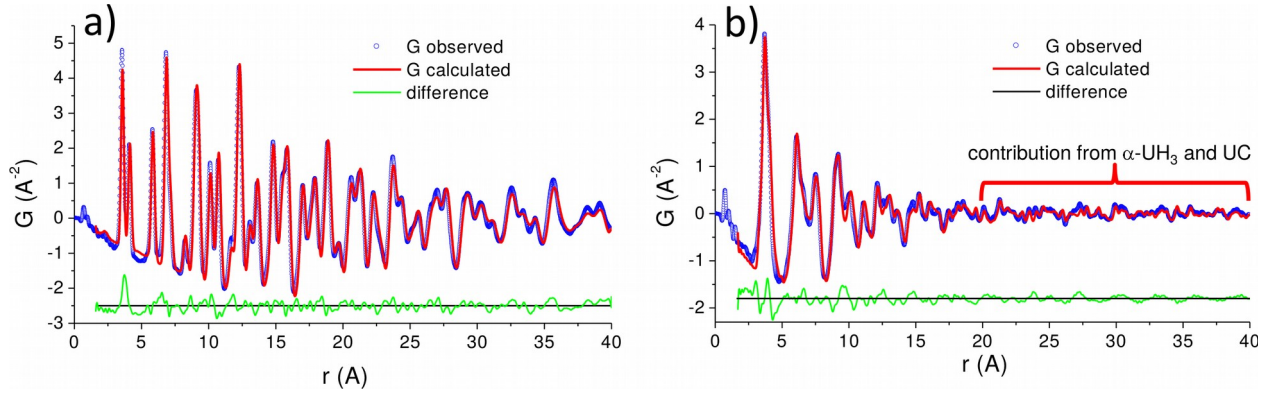

Fig. 4: PDF fits for samples (a) $(UH_3)_{0.80}Zr_{0.20}$ and (b) $(UH_3)_{0.88}Mo_{0.12}$ samples.