EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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

Reports supporting requests for additional beam time

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.

Published papers

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:** XAS Studies of the Formation of Iron Nickel Sulphides from Dithiocarbamates	**Experiment number**: 26-01-960
Beamline: BM26A	**Date of experiment**: from: 07-Sep-12 to: 10-Sep-12	**Date of report**: 01-Apr-12
Shifts: 9	**Local contact(s)**: Sergey Nikitenko Dipanathan Banerjee	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Mariette Wolthers*, Utrecht University, Netherlands

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Report:

The aim of the beamtime experiment 26-01-960, at the EXAFS beamline BM26A, DUBBLE, was to acquire local structure information during the solvothermal decomposition reaction of iron and nickel dithiocarbamates with a reducing agent, using XAS. The decomposition is a novel modification to a popular reaction for the formation of phase pure sulfides – the addition of the reducing agent changes the phase of the final product. Previous XAS results of the original reaction helped to understand the decomposition pathway. The aim here was to understand where and how the modification influenced the decomposition. This understanding brings us a step closer to understanding the process of manipulation and engineering for final product.

The decomposition of $Fe(^{i}BuDTC)_3$ and reducing agent in oleylamine, $Ni(^{i}BuDTC)_2$ and reducing agent in oleylamine, and mixed $Fe(^{i}BuDTC)_3$ and $Ni(^{i}BuDTC)_2$ and reducing agent in oleylamine, up to 200° C was observed.

The *in situ* hydro/solvothermal cell built by the Sankar group at UCL was used. A temperature calibration was performed offline to account for heatloss between heat source at base and the reaction chamber. Scan time was approximately 12 minutes per spectrum for a typical acquisition during *in situ* experiments. The data acquisition was taken during a ramp rate of 1°C/min. Reactions were held at a final temperature of 200° C, sulfide formation was shown to occur - in all cases - before the maximum temperature of 200° C and was associated with a drop in data quality due to the immiscibility of the products in oleylamine: the inhomogenous dynamic environment was an obstruction to good XAS data acquisition.

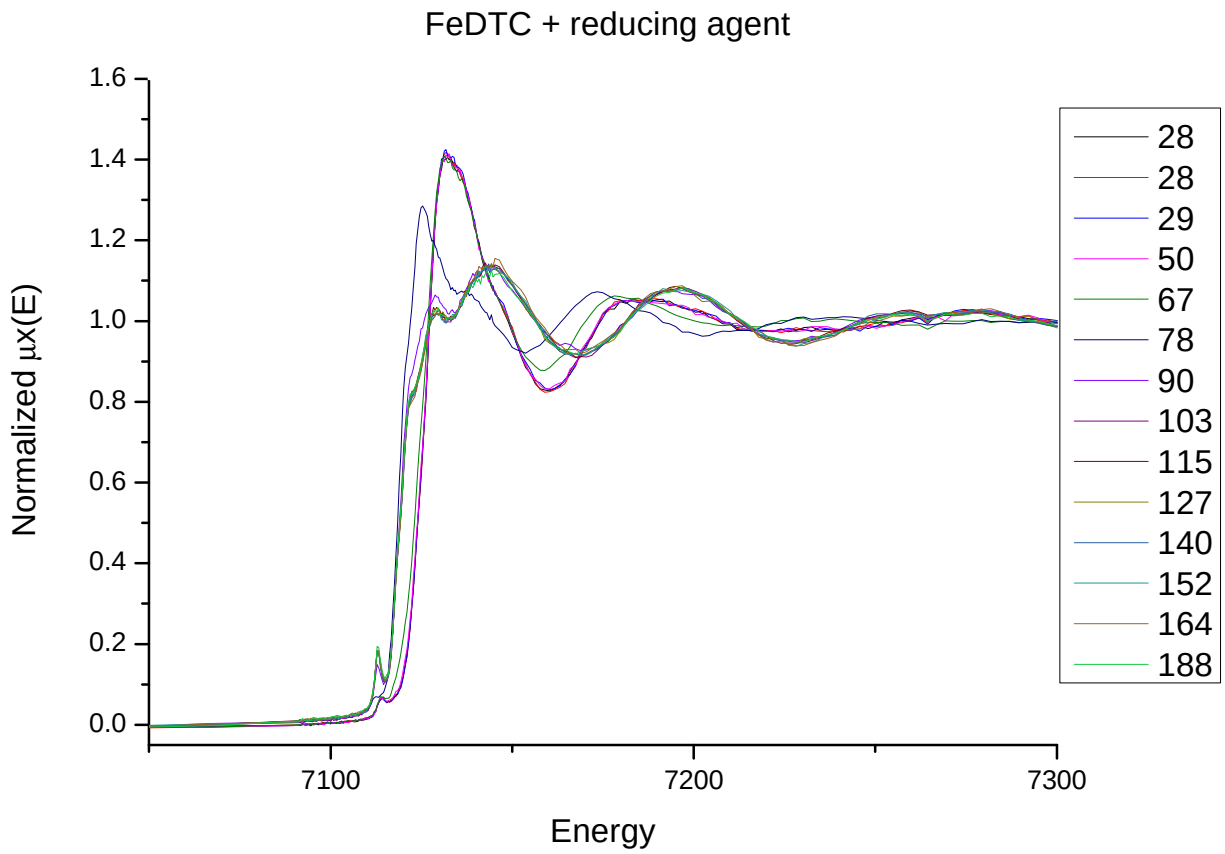

Figure 1:* in situ *XANES data of the decomposition of iron iso-butyl dithiocarbamate at a ramp rate of 1° C/min and scan time of approximately 12 minutes. Data clearly indicated a three step process.

Figure 1 shows an example of *in situ* XANES data during the decomposition of iron iso-butyl dithiocarbamate with a reducing agent. The data indicates a three stage process including change in oxidation state and formation of sulfide (a striking change in pre-edge is indicative of a geometry change. There are clear similarities and differences between this in situ result and previous results without reducing agent. The role of the reducing agent thus provides insight to what stage the precursor is partial to manipulations.

There is much knowledge to be gained through extensive analysis of the data collected, including XAFS of interesting temperatures collected after initial analysis at this beamtime, and several areas for further investigation have been decided.