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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

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:** In situ XAS/XRD studies of iron and nickel sulfide catalyst formation	**Experiment number**: 26-01-920
Beamline: BM26A	**Date of experiment**: from: 31-Oct-11 to: 04-Nov-11	**Date of report**: 21-Dec-11 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Sergey Nikitenko Miguel Silveira	

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Report:

The aim of the beamtime experiment 26-01920, at the EXAFS beamline BM26A, DUBBLE, was to acquire local structure information during the solvothermal decomposition reaction of iron and nickel dithiocarbamates, using XAS. The decomposition is a popular reaction for the formation of phase pure sulfides and thus understanding its kinetics is vitally important to be able to manipulate it.

The initial plan was to track three reactions: the decomposition of $\mathrm{Fe(^{i}BuDTC)_3}$ in oleylamine, $\mathrm{Ni(^{i}BuDTC)_2}$ in oleylamine, and mixed $\mathrm{Fe(^{i}BuDTC)_3}$ and $\mathrm{Ni(^{i}BuDTC)_2}$ in oleylamine, at temperatures between 180 and 320° C.

In the original plan, a capillary furnace for liquid media was to be built and used to perform the decompositions. During offline experiments it was realized that the cell was intrinsically unsuitable for the experiment – the liquid would be pushed out of the heat chamber and beamspot by expanding pockets of air. Instead, the *in situ* hydro/solvothermal cell built by the Sankar group at UCL was used. The highest temperatures could not be reached with the cell due to heat loss, however, high quality data was gained of before the point of iron and nickel sulfide crystallization. Scan time was approximately 12 minutes per spectrum for a typical acquisition during *in situ* experiments. The most successful data acquisition occurred at 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.

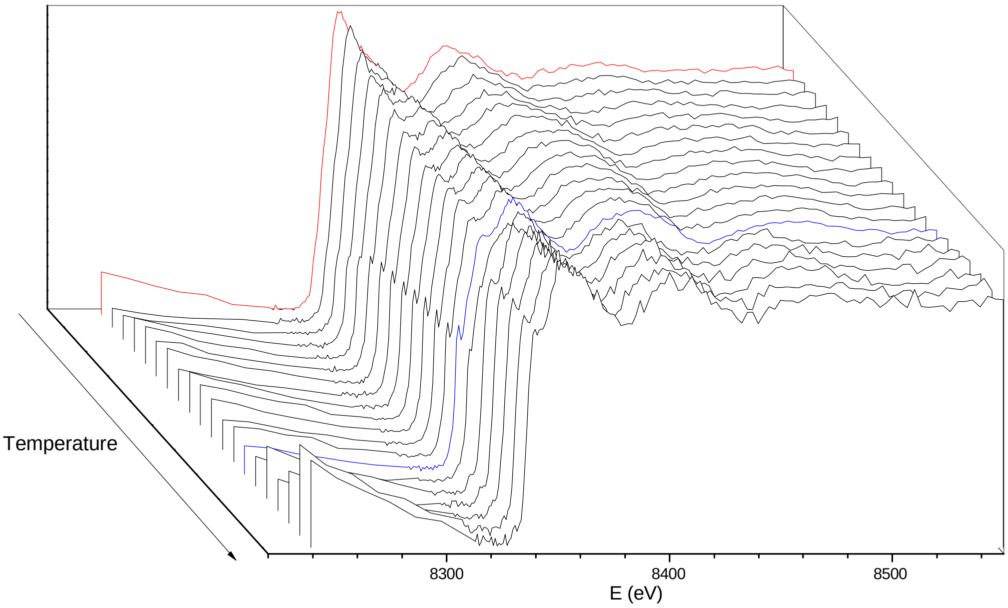

Figure 1: **in situ** ***XANES data of the decomposition of nickel iso-butyl dithiocarbamate at a ramp rate of 1° C/min and scan time of approximately 12 minutes. Data shows a gradual change in the edge between room temperature and 170° C (between red and blue) followed by an abrupt change in edge, and post edge oscillations.***

Figure 1 shows an example of *in situ* XANES data during the decomposition of nickel iso-butyl dithiocarbamate. The data indicates a two stage process: firstly, a continual change occurs between room temperature and 170° C (red to blue). This is followed by the mass formation of the sulfide which is abrupt. The pattern is unique to the nickel dithiocarbamate in both pure and mixed decompositions. Iron shows a well defined transition state at a later temperature and an edge shift associated with the formation of iron (II) species from iron (III) iso-butyl dithiocarbamate.

Several *ex situ* data were acquired of various synthesized sulfides and oxides to use as standards for linear combination fitting, and multi-component analysis. High quality EXAFS data was taken in order to perform detailed analysis for retrieving bond distances.

There is much knowledge to be gained through extensive analysis of the data collected at this beamtime, and several areas for further investigation have already been exposed. For example, one exciting prospect is to fully characterize the sulfides formed below 200° C which are known to be amorphous [1] and unassigned by XRD, once this is complete, a separate experiment can be performed to conclude phase change at higher temperatures using solid pellets rather than reaction mixtures. This will allow us to map phase against temperature and refine the reaction method for future catalytic purposes.

[1] Han, W. and M.Y. Gao, *Investigations on iron sulfide nanosheets prepared via a single-source precursor approach.* Crystal Growth & Design, 2008. **8**(3): p. 1023-1030.