EUROPEAN SYNCHROTRON RADIATION FACILITY

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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:**<br>An in situ XAS investigation of iron sulphide synthesis – precursor decomposition to nucleation and growth | **Experiment number**:<br>26-01-1019 |
| **Beamline**:<br>BM26A | **Date of experiment**:<br>from: 01-Dec-14 to: 05-Dec-14 | **Date of report**:<br>23-Fev-15 |
| **Shifts:**<br>9 | **Local contact(s)**:<br>Alessandro Longo<br>Dipanjan Banerjee | *Received at ESRF:* |


**Names and affiliations of applicants** (* indicates experimentalists):

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**Dr. Nathan Hollingsworth*, University College London, UK**

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## Report:

Outline

An *in situ* investigation using Quick EXAFS on BM26A was proposed to track the solvothermal decomposition reactions of iron tris-diisobutyl dithiocarbamate. This class of reaction is a popular synthesis technique for the formation of mono-disperse sulphide nanoparticles. While previous experiments have allowed us to uncover the precursor decomposition process, recent developments in *in situ* liquid cell design have allowed access to higher temperatures and therefore new information at the crystallisation stage of the reaction.

Cell Design

Beamline staff worked closely with Sample Environment to develope a liquid cell based on an existing cell used for pellets. The existing cell, known as the Microtron, is designed for optimum heat transfer to the sample to reduce temperature gradients and maintain temperature accuracy. The aim for the beamtime was to produce a vessel as an attachment to the furnace that could hold liquids. The most challenging aspect was choosing window materials that could be used for iron K-edge transition measurements at high temperatures. Kapton becomes soft and bulged after 150$^{o}$ C. Mica has higher glass transition and melting temperatures and thin windows can be made at 50μm width for optimum transmission, but mica contains iron impurities. The final choice in window material was quartz of 100μm width – although during the experiment these were swapped for the far cheaper glass windows of the same width, owing to breakages. The windows decrease transmission to 7% only at the iron K-edge which has meant slightly poorer data quality than with thinner windows. The glue holding windows to the aluminium frame is cement glue which has melting temperature of 270$^{o}$ C. The cell has two holes at the top which can be screwed closed.

Results

Decomposition of nickel diisobutyl dithiocarbamate in the presence of a coordinating solvent to nickel sulphide, was previously investigated by us.[1] Although the process of decomposing transition metal dithiocarbamate complexes to form nanoparticulate sulphides is well known and used frequently, the

decomposition mechanism was previously little understood. We showed that the presence of a coordinating solvent was vital for the decomposition process to occur. We also postulated the nucleation process. Iron diisobutyl dithiocarbamate decomposition results in the formation of nanoparticulate iron sulphides – these are far more relevant in the area of catalysis and goochemistry but the complexity of the system means that the decomposition is far more difficult to understand mechanistically. In previous beamtimes allocated by NWO, the decompositions were, like in the nickel case, shown to be crucially reliant on the coordinating solvent. Here, the various iron dithiocarbamate reactions were performed up to 260$^{o}$ C, and the final structure was finally observed, providing new insight into structure determination from the reaction process. Figure 1 below shows, for example, the formation of $FeS_2$ pyrite, which was formed from the decomposition of a iron diisobutyl dithiocarbamate in oleylamine in high concentrations at about 220$^{o}$ C. The full decomposition process shows four stages of decomposition and sulphide formation. Interestingly, the reaction process does not go through a less thermodynamically stable sulphide intermediate phase as originally thought. Rather, pyrite is suddenly formed at 220$^{o}$ C. This strongly suggests that the process of pyrite formation is not simply thermodynamically motivated one, and there are other factors at play, possibly including the large excess of the ligand in the reaction mixture which may act as a sulphur source.

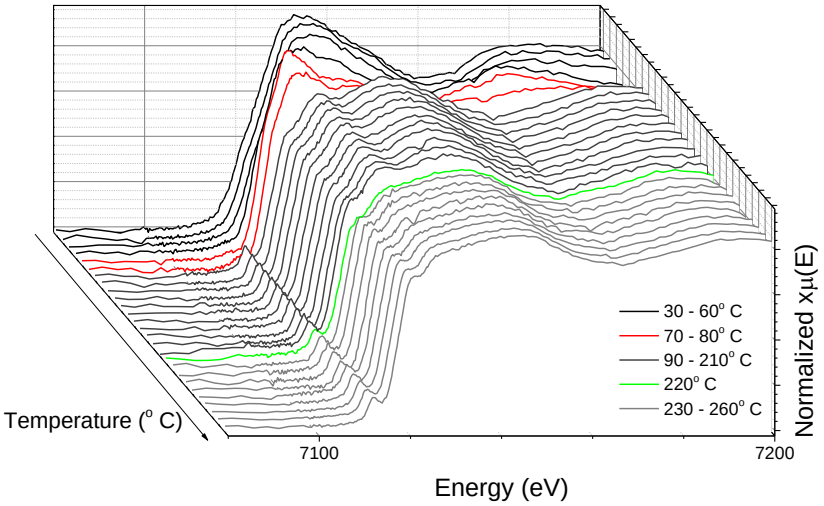


**Figure 1: In situ XANES showing the decomposition of iron diisobutyl dithiocarbamate in oleylamine. The reaction was observed up to 260º C in a modified microtron cell developed by Sample Environment at ESRF.**

Conclusions

The results of this beamtime have enabled us to further understand reaction mechanisms of a highly relevant and widely used reaction process. Results can help to tailor the process of synthesising exotic phases of sulphide material, and in the short term add to the understanding of a series of material syntheses. Before publication of these results, the full EXAFS analysis of the intermediate stages of the decomposition must be performed, and supporting characterisation techniques must be used in order to add merit to our findings which have largely only been observed by XAS owing to the nature of the system. Our aim is also to understand other single source precursor materials and their interaction with solvents and effects of reaction conditions inluding the reaction that forms molybdenum disulphide – a material used widely as engine lubricants in the fuel industry, and cadmium sulphide quantum dots, used as photodetectors and fluorescence probes.

1. Nathan Hollingsworth, Anna Roffey, Husn-Ubayda Islam, Maxime Mercy, Alberto Roldan, Wim Bras, Mariette Wolthers, C. Richard A. Catlow, Gopinathan Sankar, Graeme Hogarth, and Nora H. de Leeuw; Active Nature of Primary Amines during Thermal Decomposition of Nickel Dithiocarbamates to Nickel Sulfide Nanoparticles; Chemistry of Materials, 2014, 26 (21), pp 6281–6292