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

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Effect of High Pressure on Spin Crossover Compounds	**Experiment number**: HC-4970
Beamline: BM01	**Date of experiment**: from: 04.10.2022 to: 10.10.2022	**Date of report**: 11.09.2023
Shifts: 15	**Local contact(s)**: MC MONAGLE Charlie	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The aim of this experiment was to carry out high-pressure X-ray diffraction measurements on single crystals of two Fe(II) spin-crossover complexes. The first compound is $Fe(PM\text{-}AzA)_2(NCS)_2$, (PM-AzA=N-(2'-pyridylmethylene)-4-(azophenyl) aniline) (space group $P2_1/c$) which undergoes a gradual spin transition around $T_{1/2}$ ~189 K [1]. The second one is $Fe(PM\text{-}Bia)_2(NCS)_2$ which crystallizes in two polymorphs depending on the synthesis route. The first polymorph **Bia-P_{ortho}**, is orthorhombic (space group *Pccn*), while the other polymorph **Bia-P_{mono}**, is monoclinic (space group $P2_1/c$). **Bia-P_{ortho}** undergoes an abrupt transition around 179 K with a thermal hysteresis of 5 K, while **Bia-P_{mono}** undergoes a gradual spin transition at about 209 K [2].
The results were supposed to provide a clear picture of the transition from high-spin to low-spin state in the crystal structures of the first compound and also a better understanding of the pressure-induced phase transition between the two polymorphs of the latter compound. In addition, it is expected to provide the basis for understanding the pressure-dependent infrared spectroscopy data that we have already collected at SOLEIL (Paris) and ultimately (with further work) to establish a P-T phase diagram.

In our experimental study, we employed diamond anvil cells with different opening angles (≥85°), including our newly designed compact cells developed to work for both X-ray and neutron experiments [3]. They have a large opening angle of 120° and are made of materials suitable for neutron scattering experiments. Single crystal sizes loaded in the DAC's were of the order of 50-70 µm. In order to obtain hydrostatic pressure conditions,

isopropanol as a pressure medium was utilized, which is found to remain hydrostatic up to 4 GPa at room temperature. Measurements were performed up to a pressure of 2.2 GPa, with a pressure resolution of 0.3-0.5 GPa, each pressure point measurement consisting of two runs. The pressure was deduced by measuring the shifts in the luminescence spectra of ruby, which is the most widely used to measure in high-pressure research with the DAC. Data were collected at room temperature, employing a photon energy of 20.5 keV. An ω-scan was used for data collection, with a scan width of 0.1°.

At the lowest pressure points, we could succesfully measure the diffraction intensities on both polymorphs of the $Fe(PM\text{-}Bia)_2(NCS)_2$ compound. However, as we increased the pressure, the diffraction signal in both samples deteriorated. At present, the reason for this is unclear (interaction with the pressure media, radiation damage, pressure-induced transition).

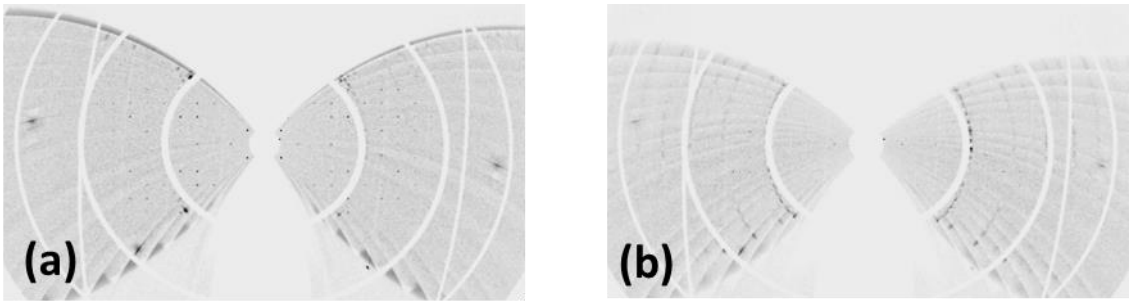

*Figure 1: The reconstruction of reciprocal space in the 0kl plane for the monoclinic polymorph of the $Fe(PM\text{-}Bia)_2(NCS)_2$ compound, at two different pressure points **(a)** 0.33(1) GPa and **(b)** 0.51(2) GPa.*

It is, however, noteworthy that, when checking the recovered samples after decompression it became evident that the recovered single crystals were cracked.

References:

[1] S. Lakhloufi, et al., *Phys. Chem. Chem. Phys*. **18**, 28307–28315, 2016.
[2] H. Shahed, et al., *Acta Crystallogr., Sect. B*, **B79**, 5, 2023.
[3] A. Grzechnik, et al., *J. Appl. Crystallogr*. **53**, 9–14, 2020.