EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

# 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:** Investigation of the electron orbital configurations in elemental Li metal under high pressure using x-ray raman scattering technique. | **Experiment number**: HC-5121 |
|---|---|---|
| **Beamline**: | **Date of experiment**: from: 25 Oct 2022 to: 01 Nov 2022 | **Date of report**: 09 March 2023 |
| **Shifts:** | **Local contact(s)**: Christoph Sahle | *Received at ESRF:* |


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

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**Report:**

Alkali metals have long been considered as prototype "simple" metals [1]. However, views on their physical properties have changed drastically over the last two decades. Studies have shown that alkali metals are not "simple" at all under high pressure conditions, showing various exotic low symmetry crystalline phases and large deviations from the nearly free electron like behaviour that eventually lead to poor metallic or even to non-metallic band structures [1-8]. Depending mostly on the theoretical calculations and a few indirect information from experimental studies, a hybridisation processes between the ***2s*** valence orbital and next higher orbital state (***p*** for Li and Na, and ***d*** for K, Rb and Cs) have been suggested to play very important role for the exotic pressure behaviour of the alkali metals [7-12]. Main goal of our proposal was to verify such a scenario using a suitable x-ray core-level spectroscopy technique that directly probes the relevant final orbital states.

For this purpose, we attempted to perform high pressure x-ray raman scattering experiments at the ID20 beamline of ESRF. Initially, the study was planned to be conducted on elemental Li as mentioned in the proposal. However, shortly before the experiment we were informed by a well known high pressure expert at ESRF (Dr. M. Hanfland) that pure elemental Li may damage the diamond anvil above 20 GPa, thus cannot be compressed easily up to the target pressure of about 80-100 GPa (we have done many literature surveys before the proposal submission, but apparently, we have overlooked such technical details). In this situation, we have decided to conduct our study on Na (another alkali element, scientific motivation and expected results were exactly the same). A screw driven panoramic diamond anvil cell with 150 um culet anvils had been prepared well before the experiment. Suitable amount of elemental Na have been loaded in to the sample chamber (~75 um diameter) of a Beryllium gasket under inert atmosphere (using the available glove box in the chemistry lab of ESRF). Unfortunately, we were not able to measure reasonable quality Na K-edge x-ray Raman scattering data, possibly because of the tiny dimension of the sample. Two different loadings have been tried, but no improvement was achieved.

In order to avoid wasting the remaining beamtime, we have decided (together with the local contact) to perform x-ray emission (XES) spectroscopy measurements on $CoTiO_3$ and $FiTiO_3$. From our preliminary high pressure XAS measurements and existing literature on these ilmenite compounds, high spin (HS) to low spin (LS) transformations are expected under pressure and association of such spin transitions with the known structural transformations needs to be investigated. As show in Fig. 1 and Fig.2, *Kβ′* emission peaks of both compounds are reduced under pressure, but not completely suppressed. Even if certain changes in the electronic configuration cannot be excluded, results imply that no complete HS to LS transition occurred in both samples within the investigated pressure ranges (up to 30 GPa). Our findings will help to improve the understanding of the phase behaviours of these ilmenite compounds. Results will be published as two independent papers in near future together with our XAS data (measured at ESRF and synchrotron SOLEIL).

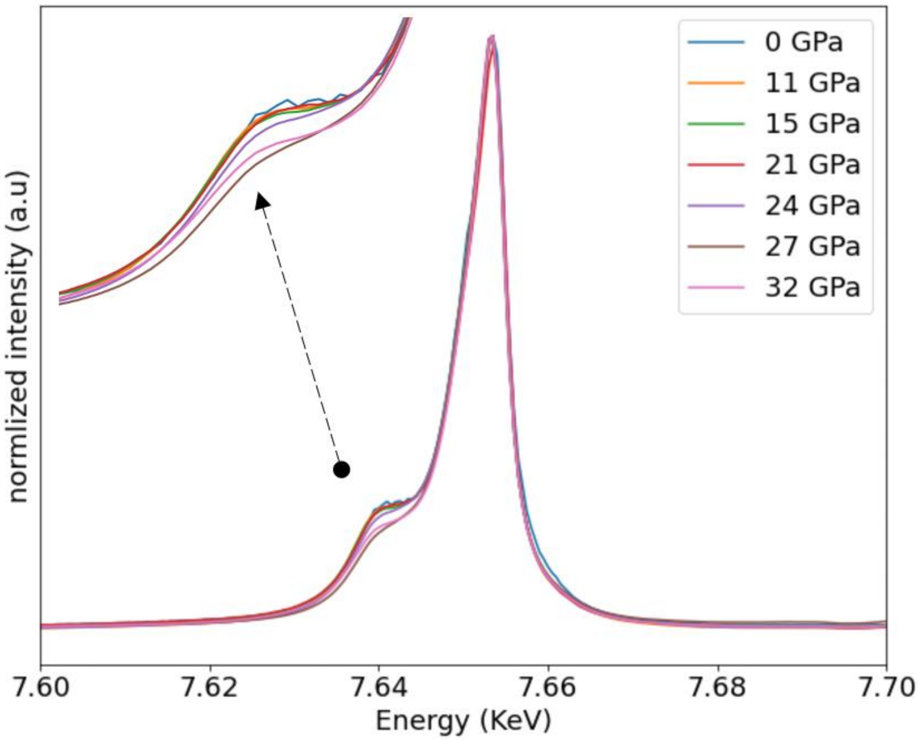


***Fig. 1 X-ray Kβ emission spectra of $CoTiO_3$***

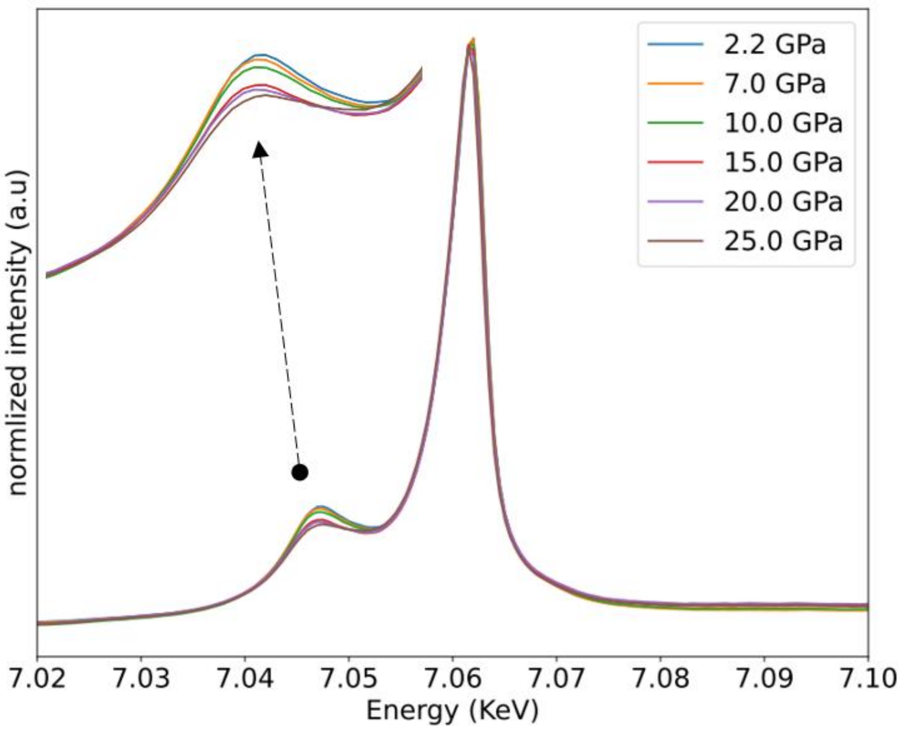


***Fig. 2 X-ray Kβ emission spectra of $FeTiO_3$***

## References:

[1] E. Wigner et al., Phys. Rev. 43, 1933.
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[6] H. Zong et al., Nature Physics, 2021. [12] A. Lazicki et al., PNAS. 106, 2009.
[7] G. Fabbris et al., Phys. Rev. B 91, 2015.
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