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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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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: "Pressure-induced Cu(I)-Fe(III) band overlap in antiferromagnetic $CuFeO_2$ delafossite".**	**Experiment number**: HE-2185
Beamline: ID24	**Date of experiment**: from: 26.04.06 to: 02.05.06	**Date of report**: 28.08.06
Shifts: 18	**Local contact(s)**: Dr. Sakura PASCARELLI, Dr. Manuel MUNOZ	*Received at ESRF:*

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Report:

High pressure XAFS experiments at the Cu and Fe *K*-edge have been performed in the antiferromagnetic insulators $CuFeO_2$ and $NaFeO_2$ to ~40 GPa. Pressures were generated with TAU oposite/plate diamond anvil cells having anvils with 300-μm diam. culets. Argon was used as a pressurizing medium. Pressure was measured using the ruby fluorescence technique. High-pressure XAFS studies were performed at beamline ID24.

The case of Cu-Fe Delafossite.

Cuprous ferrite ($CuFeO_2$) has the hexagonal layered structure which consists of hexagonal layers of Cu^{1+}, O^{2-}, and Fe^{3+}; the antiferromagnetic Fe^{3+} (S=5/2) layers are separated by nonmagnetic layers of Cu^{1+} (S=0) and O [1]. Recent High Pressure (HP) ^{57}Fe Mössbauer studies [2] detected the onset of Fe^{2+} species at around 23 GPa. For this to occur one must assume Fe^{3+} - Cu^{1+} bands overlap in which part of the $Cu^{1+} \rightarrow Cu^{2+}$ transition takes place. The obtained XAFS results indeed concurred with the Mössbauer ones, namely, changes

have been observed in both the TM cations at pressures at which Fe^{3+} - Fe^{2+} occurs. Fe *K*-edge XANES shows a clear evidence of the Fe valence state change in the pressure range 18 -31 GPa (Fig. 1a,b). Analysis of the behaviour of the pre-edge peak confirms an Fe redox variation (Fig. 1c). Analysis of the Cu *K*- edge data is currently in progress.

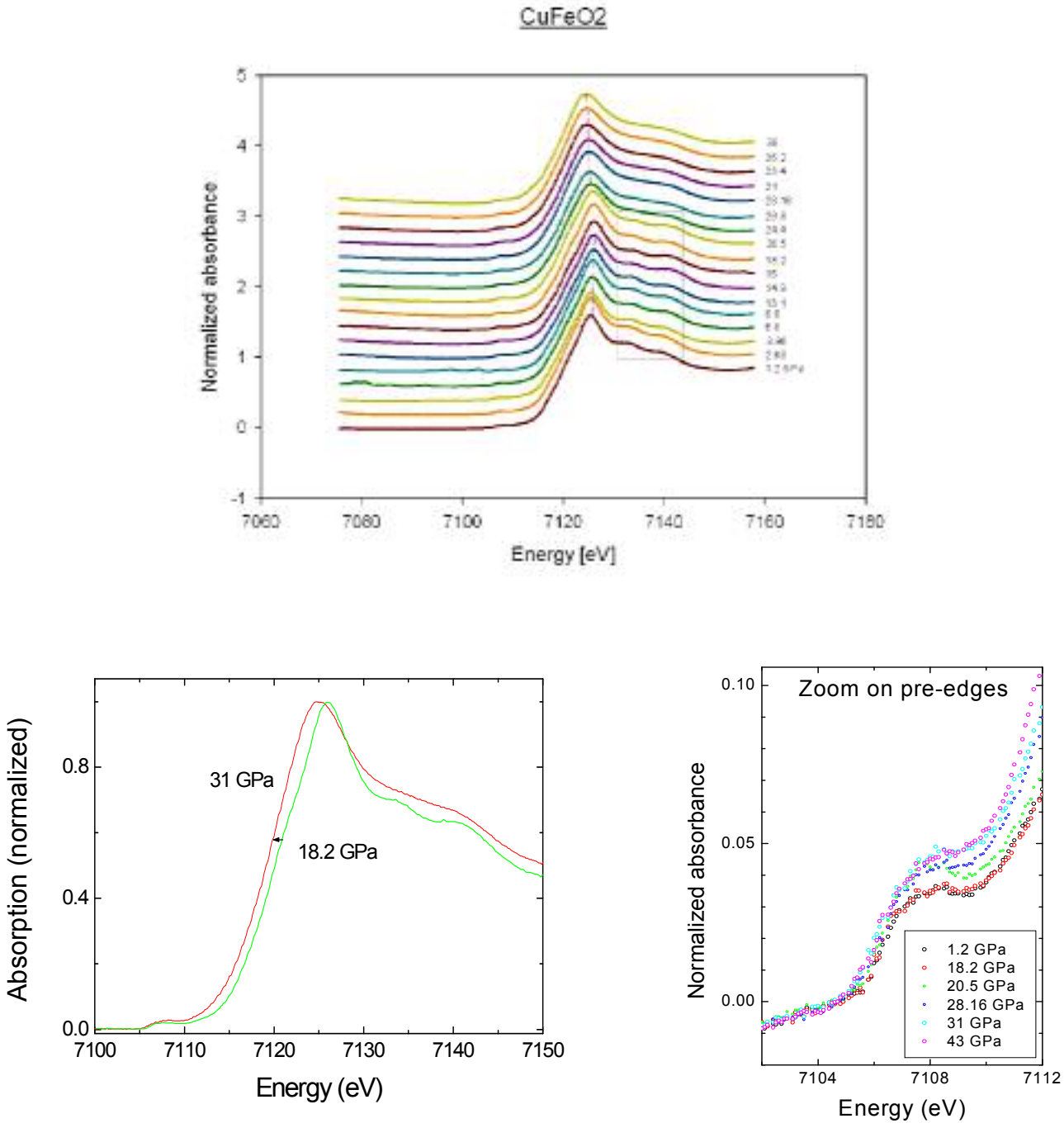

Fig.1a-c. Fe *K*- edge XANES of $CuFeO_2$, showing a clear evidence of the Fe valence state change in the pressure range 18 -31 GPa.

XRD studies show as well a structural phase transition corroborating the discussed valence transformation. According to a preliminary data analysis, the new high pressure phase can be fitted well with a monoclinic (*C1 2/m1*) structure. This is also a layered but slightly distorted hexagonal structure which in contrast to the low pressure phase accommodates two different types of Fe and Cu sites ($^1/_3$ of the Fe and Cu positions are occupied by Fe^{2+} and Cu^{2+} respectively). The Cu- and Fe- environment changes significantly at this transition and such structural changes affect the EXAFS spectrum (see Fig. 1a). Analysis of the XAFS should help clarify the modified local structure resulting from the change in the space group as derived form XRD studies.

The Na-Fe delafossite.

Whereas the Cu^{1+}- Fe^{3+} pressure-induced band overlap may result in the formation of paramagnetic Cu^{2+}, this will not be the case with alkali ions. And indeed our studies on $NaFeO_2$ ($R\bar{3}2/m$ space group) have shown that no appreciable changes in the XAFS spectrum are observed up to ~ 40 GPa (Fig. 2).

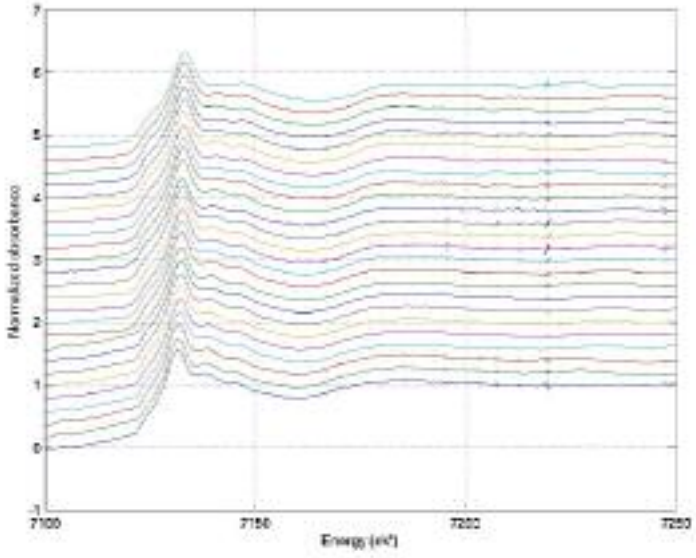

Fig. 2. Fe K- edge XANES of $NaFeO_2$ in the pressure range 3 - 44 GPa (bottom to top).

References

1 - A. Pabst, Am. Mineral, **75**, 105 (1988), M. Hasegawa, M. I. Batrashevich, T. R. Zhao, H. Takei, and T.Goto, Phys. Rev. B**63**, 184437 (2001).

2 - M.P. Pasternak, W. Xu, G.Kh. Rozenberg, M. Kertzer, H. Amiel and R.D. Taylor, invited talk (unpublished results) AIRAPT, Karlsruhe, 2005.