EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

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 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-2437
Beamline: ID24	**Date of experiment**: from: 20.06.07 to: 26.06.07	**Date of report**: 28.02.08
Shifts: 18	**Local contact(s): Dr. Sakura PASCARELLI**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Moshe P. Pasternak

Gregory Kh. Rozenberg

Yechezkel Amiel

School of Physics and Astronomy, Tel Aviv University, ISRAEL

Report:

High pressure XAFS experiments at the Cu and Fe *K*-edge have been performed in the antiferromagnetic insulator delafossite ($CuFeO_2$) to ~60 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.

$CuFeO_2$ crystallizes in the hexagonal layered structure consisting of alternating hexagonal layers of Cu^{1+}, O^{2-}, and Fe^{3+}. The paramagnetic 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] resulted in the discovery of two remarkable events: 1 – at around 23 GPa an abrupt pressure-induced (PI) reduction of the 1/3 of the Fe^{3+} ions to eventually form two magnetic sublattices of Fe^{3+} and one of Fe^{2+}, and 2 – a threefold increase in the ordering temperature T_N of the Fe^{2+} sublattice as compared with the Fe^{3+} ones. A most plausible and consistent explanation is that at a critical $\Delta V/V_0$ a sharp overlap occurs between the cuprite's and the ferric's bands resulting in the oxidation of part of the Cu^{1+}, namely:

$$\left[\overset{Fe^{3+}\ \text{sublattice}}{Cu^{+1}(S=0),\ Fe^{3+}(S=5/2)}\right] \rightarrow \left[\overset{Fe^{2+},\,Cu^{2+}\ \text{sublattice}}{Cu^{+2}(S=1/2),\ Fe^{2+}(S=2)}\right] \qquad (1)$$

The presence of two paramagnetic ions (Fe^{2+} and Cu^{2+}) in the new sublattice could explain the $Fe^{3+} \rightarrow Fe^{2+}$ mechanism and the enhanced T_N of this new magnetic sublattice.

The present HP Cu K-edge XAS [3] studies has provided additional experimental proof that indeed the process depicted in (1) is correct. Fig. 1 shows the Cu K-edge XAS spectra as a function of pressure between ambient and 45 GPa. At the edge region the ambient pressure spectrum shows a distinct peak (*A*) at the onset of absorption (~ 8984 eV), a signature of a linear O-Cu-O bonding configuration as in Cu_2O [4]. With increasing pressure to ~ 27 GPa the intensity of *A* is unchanged, after which it gradually vanishes. Fig. 2 shows the evolution of the energy position of the absorption-onset obtained from the maxima of the derivative of the absorption spectrum in the pressure range up to 27 GPa. At constant pressure and temperature the shift of the X-ray absorption onset can be related to modifications of the oxidation state of Cu, e.g., $Cu^{1+} \rightarrow Cu^{2+}$. [5] Our data show a strong positive shift in the 18- 23 GPa range in contrast with Fe which shows a negative shift, consistent with $Fe^{3+} \rightarrow Fe^{2+}$. The shift in Cu occurs in a discontinuous step, indication of a possible 1st-order phase transitions at ~ 21 GPa leveling off up to 27 GPa. This step, with an absorption-onset shift of ~ + 0.9 ± 0.1eV, is compatible with the MS data, indication that part of the cupric are transformed to cuprous ions. Based on the Fe MS data this valence transition occurs in ~ 1/3 of the Cu^{1+} resulting in Cu^{2+}/Cu^{1+} (and Fe^{2+}/Fe^{3+}) abundance ratio of 1/2.

The transition occurs not only with a positive energy shift but also with strong modifications of the near edge region,

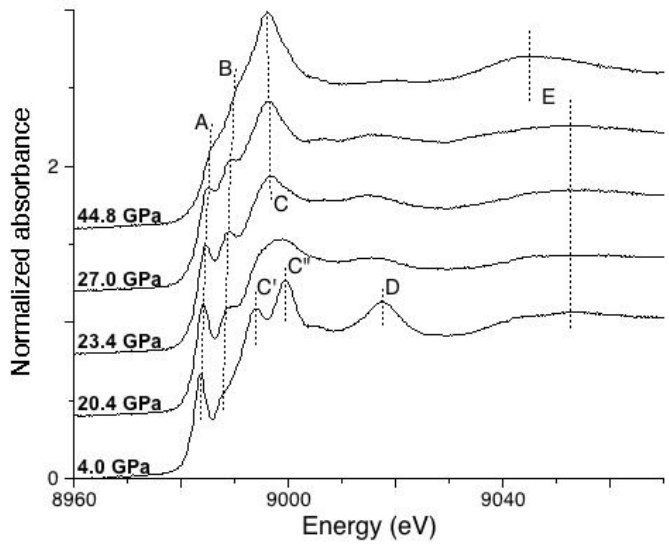

Fig.1. Cu *K*- edge XAS spectra of $CuFeO_2$, as a function of pressure.

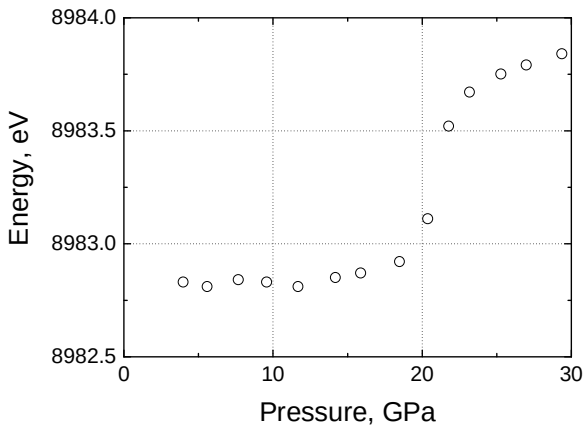

Fig. 2. The evolution of the energy position of the absorption-onset for Cu K- edge of $CuFeO_2$ in the

sensitive to the medium range order. The intensity of peak *B* around 8989 eV increases rapidly above 18 GPa; compatible with additional O atoms approaching Cu off the initial O-Cu-O direction (2^{nd} and higher coordination shells). Concurrently, peaks *C*' and *C*'' merge into peak *C* and peak *D* decreases strongly. Those changes are related to multiple scattering effects that are strongly affected by a change in medium range order. In the EXAFS region, sensitive to the first neighbors' coordination, there is no major modification of the first oscillation (*E*) up to 27 GPa. A detailed analysis shows that up to about 20 GPa, the average number of O atoms surrounding Cu is 1.8 ±0.3 and then it increases slightly to 2.5±0.2; concurrently, the Cu-O distance increases from 1.77 ± 0.02 to 1.88 ± 0.02 ´. This indicates that the phase transition following the valence changes involves a partial modification of the first coordination shell of Cu as well, and a rearrangement of the medium range structure.

X-ray diffraction studies show a structural phase transitions at ~19 GPa corroborating with the distinct step in the Cu and Fe *K*-edge shift. The new phase can well be fitted with the monoclinic (*C1m1*) structure with β angle is very close to 90^o; indicating the onset of a higher symmetry. This is also a layered structure but a slightly distorted hexagonal which can be obtained from the original low pressure phase by a distortion of the hexagonal *R-3m* cell. The transition is accompanied by a significant reduction of the *c*-parameter, crystal volume, and a sharp decrease of the *c/a* value. The reason for these alterations is the breakage of the 1/3 of the dumb-bell like O-Cu-O bonds resulting from $Cu^{1+} \rightarrow Cu^{2+}$ transition on the 1/3 of the Cu layers. A manuscript is now being prepared to be submitted to PRL.

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.

3. W. M. Xu, G. Kh. Rozenberg, M. Kertzer, M. P. Pasternak, A. Kurnosov, L. S. Dubrovinsky, S. Pascarelli, *M.* Munoz, and M. Hanfland, to be submitted to Phys. Rev. Lett.

4. We reproduced this with the ab-initio simulation – This peak corresponds to the *1s-4p*π transition. The peak B can be interpreted either as a mixture of *1s-4p*π and *1s-4p*σ transitions – see Akeyama et al., Jpn. J. Appl. Phys. **32**, 98, 1992.

5. A similar trend in the onset shift, + 3 eV, between Cu_2O (Cu^{+1}) and CuO (Cu^{+2}) has been reported by. Akeyama et al..