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 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: STRUCTURAL, ELECTRONIC, AND MAGNETIC PROPERTIES OF HIGH-PRESSURE PHASES OF THE *SPIN-FRUSTRATED* MOTT INSULATOR AFeO$_2$ (A=Cu,Li,Na).**	**Experiment number**: HS-2524
Beamline: ID09A	**Date of experiment**: from: 19.11.04 to: 23.11.04	**Date of report**: 28.02.06
Shifts: 12	**Local contact(s)**: Dr. Michael Hanfland	*Received at ESRF:*

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Report:

Structural properties of the antiferromagnetic insulators $CuFeO_2$ and $NaFeO_2$ were studied by synchrotron x-ray diffraction to 50 and 35 GPa, respectively, using diamond anvil cells. Pressures were generated with the TAU oposite/plate diamond anvil cells having anvils with 300-μm diam. culets. Argon was used as a pressurizing medium. Angle-dispersive mode high-pressure XRD studies were performed at the ID09A beam-line, diffraction images were collected with a MAR345 detector. The image data were integrated using the FIT2D program [1], and the resulting diffraction patterns were analyzed with the GSAS [2] program. Pressure was measured using the ruby fluorescence technique and Au or Pt XRD markers.

The case of Cu-Fe Delafossite. Cuprous ferrite (CuFeO2) has the hexagonal layered structure $R\bar{3}m$ which consists of hexagonal layers of Cu^{1+}, O^{2-}, and Fe^{3+} (see Fig 1); the antiferromagnetic Fe^{3+} (S=5/2) layers are separated by nonmagnetic layers of Cu^{1+} (S=0) and O [3]. At ambient pressure spins are highly frustrated between neighboring layers as well as within layers but at ~18 GPa CuFeO2 becomes a normal antiferromagnet [4]. Recent High Pressure (HP) ^{57}Fe Mössbauer studies [5] detected the onset of Fe^{2+} species at around 23 GPa. The $Fe^{3+} \rightarrow Fe^{2+}$ process has been attributed to Cu-Fe band overlap resulting in the Cu^{1+} - Cu^{2+} counter process. X-ray diffraction studies showed that the low pressure (LP) structure is stable up to ~ 16 GPa and that in agreement with Zhao et al. [6] the *a*-axis is approximately four times more compressible than the *c*-axis (Fig. 2). This is undoubtedly a unique case of an ambient pressure highly anisotropic *Mott* insulator which anisotropy further **increases** with pressure; i.e., $d(\mathrm{c/a})/d\mathrm{P} > 0$. With further pressure increase two appreciable structural transformations (Fig. 3) are detected corroborating with: *(i)* transition to a normal antiferromagnet at ~ 18 GPa, and *(ii)* valence transformation at ~ 23 GPa. These PI transitions are reversible in pressure. According to preliminary data analysis the HP phase has similar to LP phase hexagonal

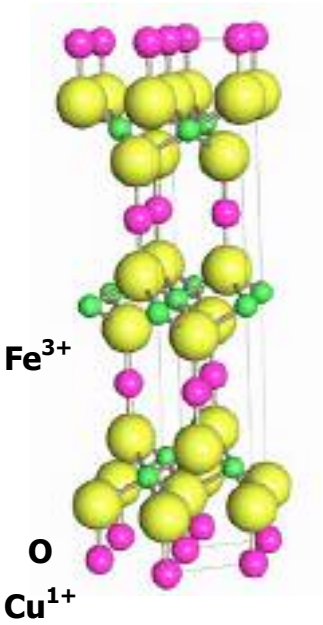

Fig.1. The structure of the layered delafossite $CuFeO_2$ at ambient pressure

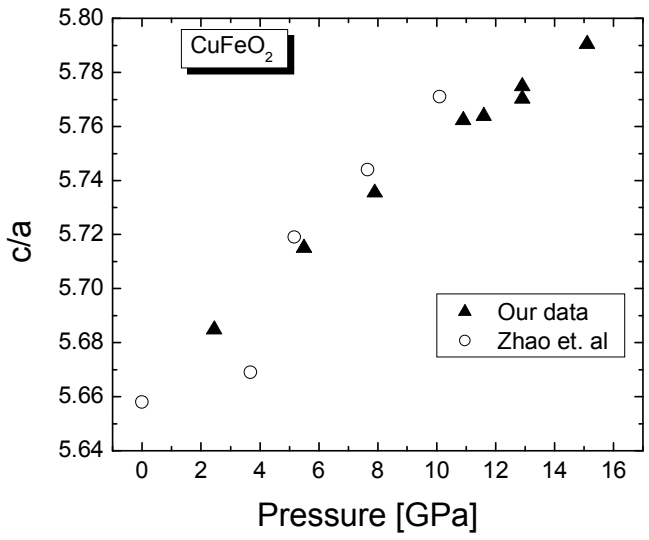

Fig. 2. Pressure dependence of *c/a* ratio for $CuFeO_2$.

layered structure but in contrast to the $R\bar{3}m$ space group, it accommodates **two different types** of Fe and Cu sites where 1/3 of the Fe layers are occupied by Fe^{2+}. Unfortunately strong peak broadening accompanying these transitions does not allow precise structural identification.

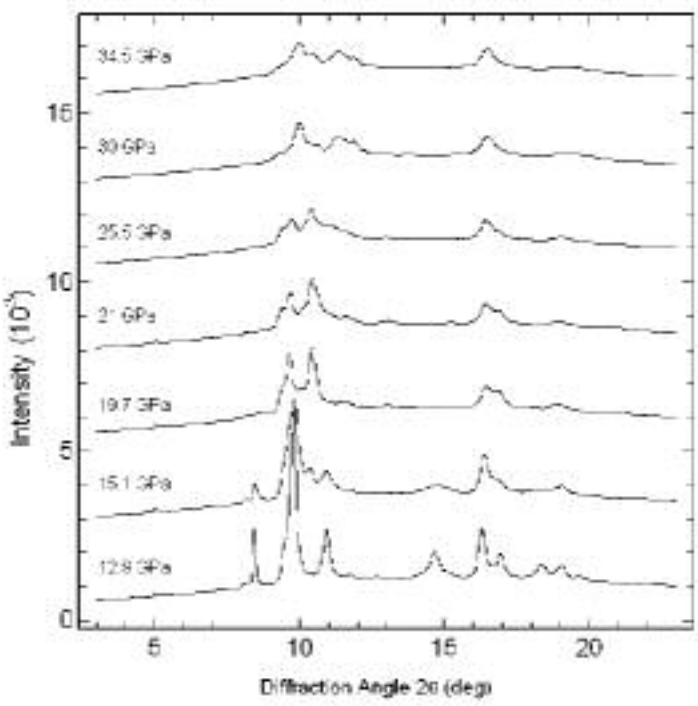

Fig. 3. XRD patterns of $CuFeO_2$ at different pressures.

The Na-Fe delafossite. Whereas the Cu^{1+}-Fe^{3+} PI band overlap may result in the formation of paramagnetic Cu^{2+}; this will not be the case with alkali ions. Our studies of NaFeO2 ($R\bar{3}2/m$ space group) have shown an isostructural transition at P~11 GPa accompanied by significant alteration of the oxygen positional parameter value, *c/a* parameters ratio (Fig. 4), and increase of bulk modulus value. The Fe-O bond length show substantial increase corroborating with a reduction of Na-O bond length. This result is rather unexpected taking into account the allowed valence states of Na. Further carefull studies of the effect of replacing monovalent Cu with Na, Ag and Li extended to higher pressures are desirable taking into account our results obtained for $NaFeO_2$.

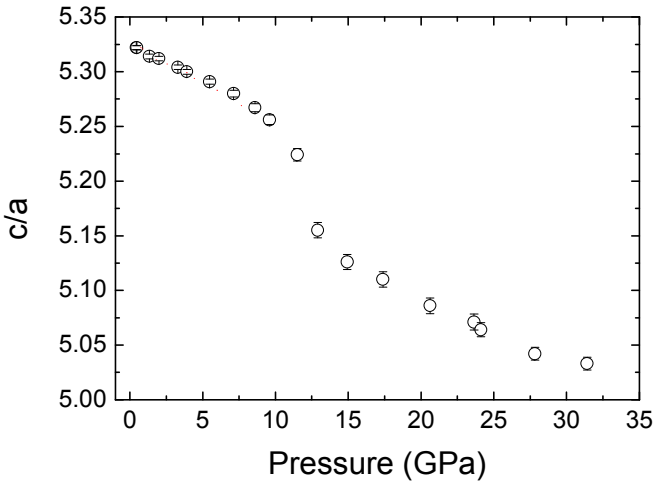

Fig. 4. Pressure dependence of *c/a* ratio for $CuFeO_2$.

References

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