



	Experiment title: High pressure XAFS on monocrystalline and powder CuAlO ₂	Experiment number: HS-2412
Beamline: ID24	Date of experiment: from: 07-07-2004 to: 12-07-2004	Date of report: 25-02-05
Shifts: 15	Local contact(s): High pressure XAFS on monocrystalline and powder CuAlO ₂	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr Julio PELLICER-PORRES* Dr. Chantal FERRER* Professor Alfredo SEGURA* Dr. Jean-Claude CHERVIN Don KIM Dr. Domingo MARTINEZ		

Report:

We have studied the structural evolution of the $CuAlO_2$ delafossite under high pressure by means of XAS measurements at the Cu K-edge (8.979 keV). High pressures were generated with a diamond anvil cell. Pressure was measured using the fluorescence of a ruby chip. Combined horizontal and vertical focalization yielded a $13 \times 25 \mu m^2$ x-ray spot.

We performed four experiments. In the first two we filled the gasket hole with the sample in powder form and silicon oil as pressure transmitting medium. The maximum pressure attained was 47 GPa.

In the other two experiments we introduced $CuAlO_2$ monocrystals, oriented in such a way to discriminate between directions parallel and perpendicular to the crystallographic c-axis by means of beam polarization (see Fig. 1). In the first monocrystal experiment we employed neon gas as pressure transmitting medium, whereas in the second one we employed silicon oil. The crystal sizes were $53 \times 80 \mu m^2$ and $60 \times 80 \mu m^2$. We obtained high quality data in both polarizations up to the maximum pressure attained, 47.9 GPa.

Dichroism is clearly observable in Fig. 1. In a previous powder experiment in the related compound $CuGaO_2$, we observed intensity variations, previous to the phase transition, which we interpreted as due to preferential orientation effects. This interpretation must be rethought, as we detect intensity variations for $P \parallel c$ from the beginning of the experiment with monocrystalline samples .

We observe for the first time a phase transition taking place, approximately, at 37 GPa. At this pressure the XANES part of the spectrum changes, specially for $P \perp c$. The phase transition is not reversible. Interestingly, the recovered spectrum for $P \parallel c$ differs completely from the original one, whereas in the perpendicular direction the recovered spectrum is similar.

From the EXAFS part of the spectrum at both polarizations it is going to be possible to follow the full structural evolution of the low pressure phase. The Cu-O Debye-Waller behavior will be of special interest to detect precursor effects, since we think that the phase transition is accompanied by shifts of AlO octahedra layers implying a change in Cu coordination.

Thanks to the efforts of the local contact, who prepared the experimental set-up before we arrived, we had extra time at the end of the experiment to take spectra of additional samples. We measured the XANES spectra of $CaWO_4$, $SrWO_4$, $BaWO_4$ and $PbWO_4$ scheelites up to 20 GPa, at the W L-III edge. There is some controversy in the literature about the nature of the high pressure phase of $CaWO_4$. Two possible high pressure phases have been suggested, fergusonite and wolframite. In the scheelite structure the W environment is formed by four oxygen atoms in tetrahedral configuration. If the high pressure phase is fergusonite, the tetrahedron would become distorted, giving rise to two slight different distances, but the main characteristics of the W environment would be maintained. In this situation we expect small changes in the XANES spectra. If, on the opposite, the high pressure phase transition originates a wolframite-type phase, the W coordination would change to six (2+4), and appreciable changes in the XANES features are expected. From the experimental spectra (see Fig. 2) we conclude that the high pressure phase is fergusonite.

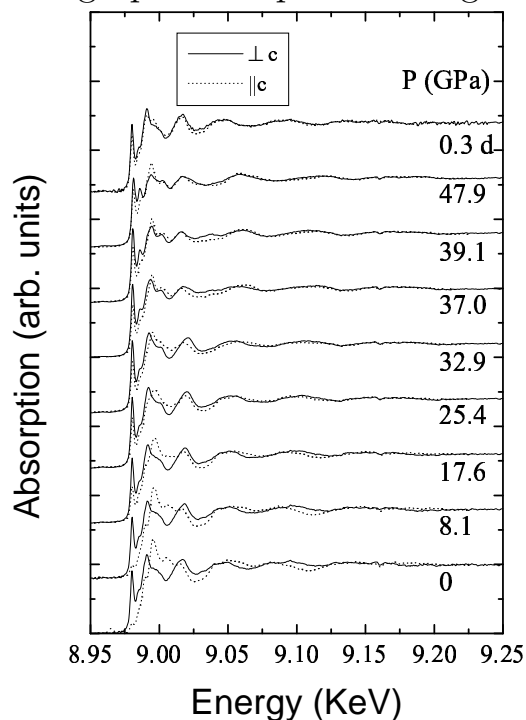


Fig. 1. XAS spectra of the $CuAlO_2$ delafossite at the Cu K-edge. A phase transition is observed at 37 GPa. Continuous and dotted lines indicate beam polarization perpendicular and parallel to the crystallographic c-axis.

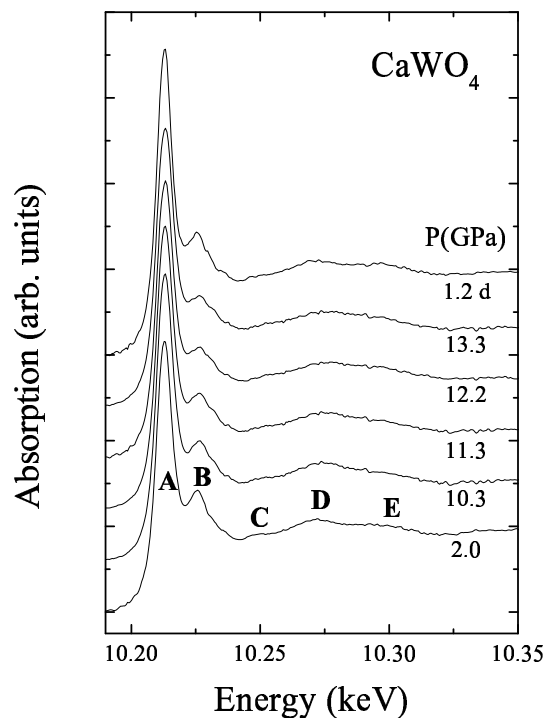


Fig. 2. XAS spectra of the $CaWO_4$ scheelite at the W LIII-edge. The analysis of the spectra reveals a transition to the fergusonite phase. The phase transition begins at 11.3 GPa.