ESRF	**Experiment title:** Pressure-induced structural and charge-transfer transition in $CuReO_4$	**Experiment number**: HS4595
Beamline: ID09A	**Date of experiment**: from: 11.07.2012 to: 14.07.2012	**Date of report**: 01.03.2013
Shifts: 9	**Local contact(s)**: Michael Hanfland	*Received at ESRF:*

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Report:

The experiment HS-4595 was aimed at the structural investigation of $CuReO_4$ under high pressure. At ambient conditions, this compound is a diamagnetic insulator ($Cu^{+1}Re^{+7}O_4$) with the tetragonal crystal structure (space group $I4_1cd$), while hydrostatic pressure leads to a drastic reduction in the band gap, and may eventually induce a charge-transfer valence transition toward the $Cu^{+2}Re^{+6}O_4$ phase. Our Raman study demonstrates a disappearance of the Raman signal above 7 GPa, where $CuReO_4$ likely becomes metallic.

During the synchrotron experiment, we have studied room-temperature structural behavior of the powder sample of $CuReO_4$ in diamond anvil cells from ambient pressure up to 20 GPa. Two reversible phase transitions were observed in this pressure range (Fig. 1). Both transitions preserve the tetragonal symmetry of the material. Additionally, single-crystal diffraction experiments were performed up to 4.5 GPa. Unfortunately, single-crystal experiments at higher pressures were not possible due to the breaking of crystals.

The ambient-pressure polymorph of $CuReO_4$ is stable up to 1.8 GPa, in agreement with our laboratory XRD data. It shows a highly unusual compression behavior, with the decreasing parameter *a* and the increasing parameter *c* (Fig. 1).

Above 1.8 GPa, a significant reduction in the cell volume, a drastic increase in the *a* parameter and a decrease in the *c* parameter are observed. The sample color changed from orange to black, thus indicating a major structural transformation towards the first high-pressure polymorph HPI. Previously, we believed that this transformation is isosymmetric, because reflection conditions in the laboratory single-crystal data for HPI were consistent with the $I4_1cd$ space group. However, both single-crystal and powder data collected at the ESRF show two strong Bragg reflections (001) and (051) that violate the $I4_1cd$ symmetry, see Fig. 2. We believe that our lab data were skewed, perhaps due to a mistake in the absorption correction. The good match between the powder and single-crystal data collected at ESRF leaves no doubt that the AP and HPI polymorphs have different symmetries. The new data suggest that HPI has the $I4_1/a$ symmetry. The pressure evolution of the lattice parameters is somewhat unusual, with the *c* parameter showing a weak but well-defined maximum around 4 GPa.

The formation of the second high-pressure polymorph (HPII) above 7 GPa was accompanied by an abrupt shortening on both *a*- and *c*-parameters, see Fig. 1. The powder pattern of HPII is also consistent with the $I4_1/a$ symmetry. Therefore, the HPI-HPII transition is likely isosymmetric.

Thus, our synchrotron diffraction experiments corrected a mistake in our earlier laboratory data and provided indispensable information on the pressure evolution of $CuReO_4$. The structure solution for HPI and HPII polymorphs is still in progress, because we were unable to achieve good powder statistics, hence a careful analysis of the data and an input from other methods are required. Nevertheless, we hope that plausible structural models can be constructed and used in further work on $CuReO_4$, including optical measurements at high pressures and electronic structure calculations for different polymorphs.

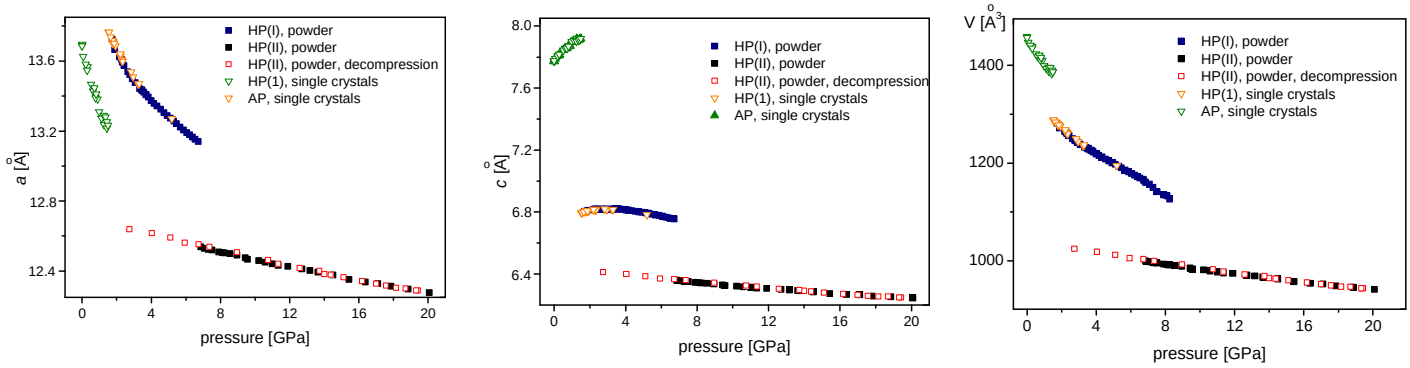

Figure 1. Pressure dependence of lattice parameters measured upon compression and decompression on both single crystal and powder of $CuReO_4$.

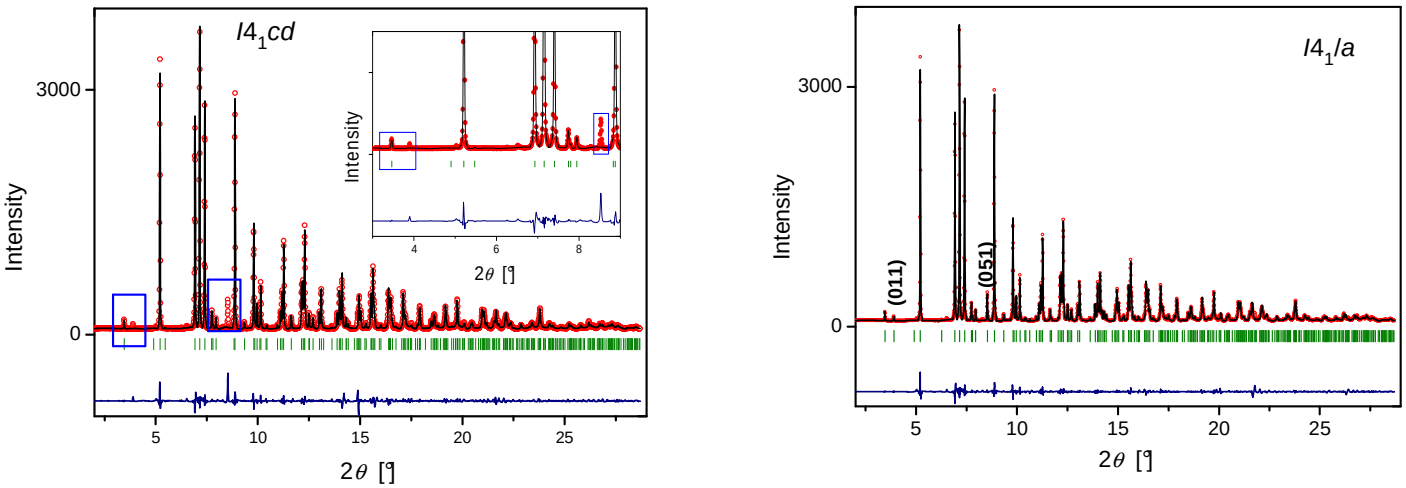

Figure 2. Diffraction pattern of the first high-pressure polymorph of $CuReO_4$ at 1.73 GPa. Two notable Bragg reflections at 2θ = 3.9° and 8.7° are inconsistent with the $I4_1cd$ space group (left) and imply the $I4_1/a$ or lower symmetry (right).