| ESRF | **Experiment title:** High pressure synchrotrons x-ray powder diffraction study of high temperature superconducting Hgcuprates | **Experiment number:** HC-171 |
|---|---|---|
| **Beamline:** ID9-BL3 | **Date of experiment:** from: 02-APR-95 07:00 to: 08-APR-95 07:00 | **Date of report:** 23-feb 96 |
| **Shifts:** 12 | **Local contact(s): Daniel HAUSERMANN** | *Received at ESRF:* |

**Names and affiliations of applicants (* indicates experimentalists):**

**P. BORDET*, Cristallographie, CNRS Grenoble, and ESRF**
**R. HADFIELD*, Cristallographie, CNRS Grenoble**
J.J. CAPPONI, Cristallographie, CNRS Grenoble
M. MAREZIO, Cristallographie, CNRS Grenoble
M. HANFLAND*, ESRF
D. HAUSERMANN*, ESRF

**Report:**

The Hg-cuprate superconductors are known to display a very strong increase of Tc with applied pressure, with a record Tc of ≈ 160 K for Hg- 1223 at pressures above 25 MPa. The goal of the present experiment was to measure the evolution with applied pressure of the structure of three members of this series, namely the 1201, 1212 and 1223 compounds, and to determine which are the relevant structural parameters governing this dramatic behaviour. Two different Hg- 1201 samples with different oxygen doping levels (one underdoped non superconducting sample and one optimally doped sample with Tc ≈ 90K) were also measured in order to detect possibly different evolutions with pressure as a function of doping.

The experiment was carried out in the monochromatic mode at a wavelength of 0.38Å. Imaging plates were used as detectors. The samples (well characterized finely grounded powders) were mounted in the diamond anvil cells together with ruby grains used for internal pressure calibration, which was performed in situ. Silicon oil or cryogenically loaded argon were used as pressure transmitting media. 74 diffraction patterns were recorded for four different samples at pressures up to ≈ 22 GPa. Wavelength and sample-plate distance calibrations. were obtained from a silicon powder image.

The spatial distortion and tilt corrections, and the Debye ring averaging allowing to avoid preferred orientation and grain effects were carried out using the fit2D program. This procedure yielded a set of powder diffractograms which were further used as input data for Rietveld refinements using the Fulprof program.

During the experiment, it soon appeared than some of the Bragg peaks were considerably broadened with increasing pressure, while others (hkO and 001) remained narrow. This behaviour became noticeable at higher pressures for higher members in the series. Further inspection of the diffractograms indicated that reflexions were not only broadened, but also displaced, which made an accurate indexing of the high pressure patterns difficult and considerably hindered the refinements. Inspection of the raw images indicated that the line broadening was isotropic along the Debye rings and did not result from, for example, an inaccurate spatial distortion correction followed by ring averaging. This effect is attributed to the large anisotropy of the unit cell contraction along the c axis coupled to the anisotropy of the applied pressure.

In order to overcome this difficulty, the Rietveld refinements were carried out using an empirical model to take into account the anisotropic peak shifts, which we implemented in the Fulprof refinement program. This treatment allowed us to obtain satisfactory fits up to the highest pressures for the three samples. However, an accurate determination of the positional parameters of the oxygen atoms at high pressure values was not possible due to the very large peak overlap resulting from the broadening of reflexions. Nevertheless, this new method of refinement yielded reliable cell parameter values up to the highest pressures, despite the anisotropic peak shift effect.

The analysis of the refinements, although still in progress, indicates that the main effect of pressure is to shorten very rapidly the c parameter through a very strong decrease of the Cu-O apical bond, which is known to be, at room pressure, the longest apical bond among all superconducting cuprates.

The “external users” would like to take this opportunity to stress the great competence and disponibility of the high pressure team at the ESRF.