| | Experiment title: Oxidation states of $FeO_2$ and $FeO_2H_x$ at high pressure | Experiment number: ES-693 |
|---|---|---|
| Beamline: ID-24 | Date of experiment: from: 30/11/2017 to: 03/12/2017 | Date of report: |
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## Report:

In this report, we present additional XANES measurements at the Fe K-edge collected on iron oxides in order to determine the iron oxidation state in the newly discovered phases $FeO_2$ and $FeO_2H_X$ (see experimental report ES-693 for beamtime from 01/11/2017-07/11/2017).

XANES spectra were measured *in situ* at high pressure and temperature through laser heated diamond anvil cell on the ID-24 beamline at ESRF.

It was recently proposed that subduction of hydrathed material down to the core mantle boundary could react with the metal Fe from the core to form he pyrite-structured $FeO_2H_X$ (with $0 < x < 1$) (Mao et al., 2017). $FeO_2H_X$ would represent a possible candidate for the peculiar seismic signature observed down at the core mantle boundary : the ultra-low velocity zone (ULVZ) (Liu et al., 2017).

Here we measured XANES at Fe K-edge upon the transformation of wustite (FeO) loaded into $H_2O$. We used diamond culet of 150 µm. Pressure was measured before and after the laser-heating cycle using either Raman shift from the diamond tip (Occelli, Loubeyre, and LeToullec 2003). We first compressed to ~50 GPa and transformed the sample at 1500 K. As presented in Figure 1; the Fe K-edge measured after laser heating is closed to FeOOH at ~50 GPa. As evidenced by the change of position of the Fe K-edge , this synthesization comes with oxidation of $Fe^{2+}$ (in the FeO) into $Fe^{3+}$ (as in FeOOH). We then compressed the sample to ~90 GPa and transformed it at 2150 K. We observed modification Fe K-edge, however the new spectrum is different from the Fe K-edges collected upon transformation of FeOOH at similar pressure and temperature in previous experiments (Figure 2). Interpretation of this new spectroscopic signature is still under progress.

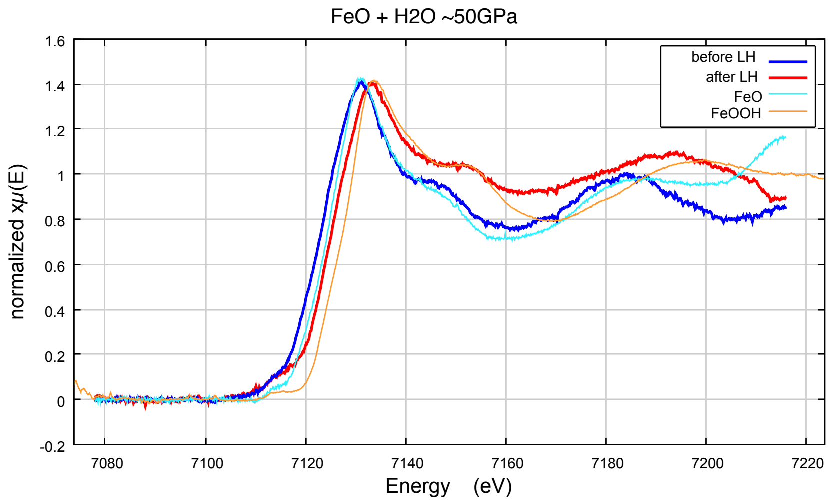


**Figure 1:** Fe K-edge spectra collected before and after laser heating (LH) upon the transformation of FeO + $H_2O$ at 50 GPa. Are given, as references, spectra collected at the same pressure of FeO and FeOOH.

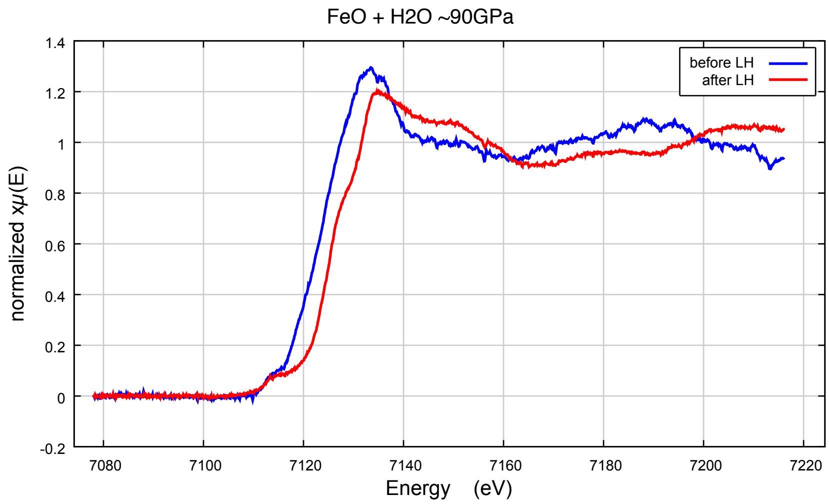


**Figure 2:** Fe K-edge spectra collected before and after laser heating (LH) upon the transformation of FeO + $H_2O$ at 90 GPa.

Two more experimental runs were performed as "standards at high pressure et temperature" . We first collected Fe K-edge spectra on FeO loaded between two layers of dried KCl discs which serves as thermal insulator and pressure medium. We collected XANES spectra upon compression up to 80 GPa and laser heating up to 2500 K. No modification of the Fe K-edge after laser heating was observed. We finally collected XANES spectra upon compression of $FeS_2$ loaded into KCl up to 85 GPa. We measured first experimental evidence of metallisation of $FeS_2$ above 80 GPa (Figure 3). No further modifications were observed upon laser heating.

Further analyses on the pre-edge of Fe K-edge are in progress. Together with the results from the beamtime (01/11/2017 – 07/11/2017), this experimental work leads to two scientific publications which are in preparation, a short one to report the metallisation of $FeS_2$ above 80 GPa and a second to discuss the oxidation state of iron in the new pyrite-structured oxides.

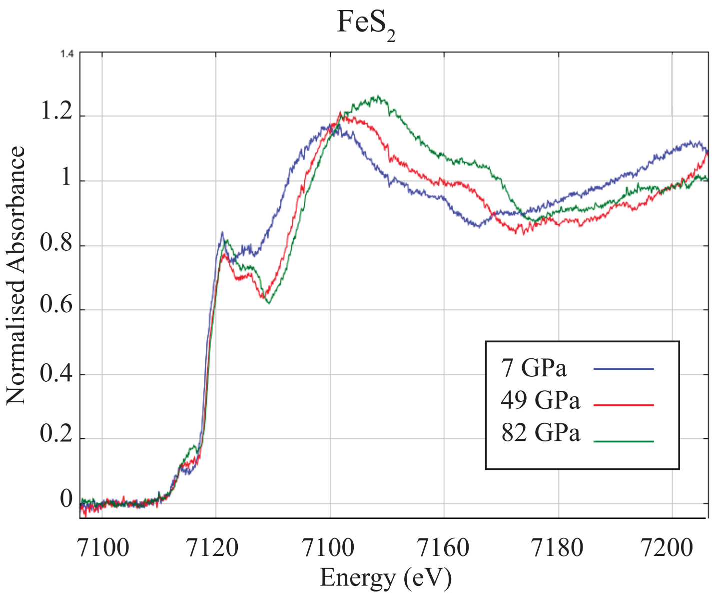


**Figure 3:** Fe K-edge collected upon compression at room temperature of $FeS_2$. Strong modification in the pre-edge can be observed above 82 GPa as a result of mettalisation of $FeS_2$ at these pressure conditions.

**References:**

Liu, J., Hu, Q., Young Kim, D., Wu, Z., Wang, W., Xiao, Y., Chow, P., Meng, Y., Prakapenka, V.B., Mao, H.-K., and Mao, W.L., 2017, Hydrogen-bearing iron peroxide and the origin of ultralow-velocity zones: Nature, v. 551, p. 494–497, doi: 10.1038/nature24461.

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Occelli, Florent, Paul Loubeyre, and René LeToullec. 2003. "Properties of Diamond under Hydrostatic Pressures up to 140 GPa." Nature Materials 2 (3): 151–54., doi:10.1038/nmat831.