ESRF	**Experiment title:** Structure and phase transitions of solid and liquid Fe nanoparticles at high temperature	**Experiment number**: 08-01-891
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Report:

Within this experiment we have used x-ray absorption spectroscopy (XAS) for an in-situ study of Fe nanoparticles embedded in amorphous dielectrics (SiO_2, Al_2O_3) at high temperature. The aim of the proposal was twofold:

1) to map the Fe bcc→fcc transition (occurring at 1183 K in the bulk phase) following changes in the absorption spectra.

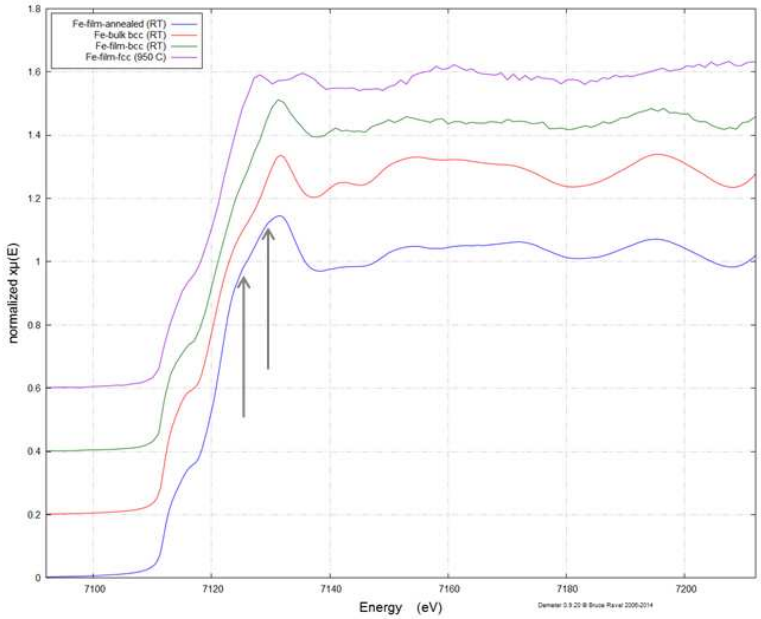
In a previous preliminary experiment (GILDA beamline, in-house research), preliminary grazing-incidence x-ray diffraction on Fe clusters in silica has shown that the bcc to fcc Fe phase transition does not occur at least up to 1450 K. This is in agreement with the results obtained on cobalt nanoparticles embedded in silica (HS-1866, grazing incidence x-ray diffraction on the GILDA beamline), for which the hcp→fcc martensitic phase transition of Co occurred at about 1100 K instead of 695 K of the bulk phase.

2) to collect XAS spectra of molten Fe in order to investigate the local structure. This has been been successfully done for other liquid transition metals such as Cu, Ni, etc, although the study of molten Fe is even more challenging because of the extreme temperature (> 1808 K) required to access the liquid phase.

Within the allocated beamtime, we have investigated three classes of samples (prepared at the Dept. of Physics-Univ. Padova, Italy)

a) a 5 μm thick Fe foil;
b) a thick (≈ 150 nm) Fe layer deposited on silica and capped with an alumina layer;
c) Fe nanoclusters in silica prepared by ion implantation and subsequent annealing (dose $1x10^{16}$ Fe at/cm^2)

For XAS measurements under high temperature conditions, we have installed on the beamline a resistive heating furnace. The sample was mounted within a graphite crucible and a Pt/Rh thermocouple was placed aside, close to the sample. The furnace fits the second vacuum chamber on BM08 and allows measurements in transmission as well as in fluorescence mode up to 1850 K according to preliminary tests.
We have used some beamtime for the furnace installation and to optimize the geometry to minimize the sample to detector distance. Because of geometric constraints of the vacuum chamber, such distance could not be reduced to less 20 cm which results in a too low solid angle of detection to perform measurements on the more diluted samples (ion implanted Fe clusters). Thus, the *in-situ* experiment could be successfully performed only for bulk Fe and for a thick (≈ 150 nm) Fe layer deposited on silica and capped with an alumina layer. All the other samples were heated ex-situ at defined temperature (between 1073-1173 K) for a few hours and then measured at room temperature on the standard vacuum chamber allowing a smaller sample to detector distance (larger collection angle). Because of the time needed to setup the furnace and to peform the annealing of the samples to be succesively measured ex-situ, we focused on the first part of the proposal and the envisaged highest temperature needed to measure molten Fe was not reached.
XANES spectra were recorded for Fe foil and for the Fe layer sample at selected temperatures, during the heating and cooling ramps in vacuum. The maximum achieved temperature was 1523 K.
About the Fe layer heated in-situ, we have observed the bcc-fcc phase transition at about the same temperature as in bulk (green and purple lines in the figure below). Nevertheless, after long time vacuum annealing (a few hours) at 1173 K the transition was inhibited. When this occurs, a slight modification of the XANES spectrum was observed, marked by the two arrows in the figure (blue spectrum), to be compared with the spectrum of bcc Fe bulk (red line) and to the one of bcc film (green line). From an XRD characterization performed on the recovered samples, no other crystalline phases were found besides Fe bcc. The XANES modification is likely due to a modification of the Fe site at the nanostructure interface. The other samples measured ex-situ seem to present the same modification.



Work is in progress to understand these results. Future experiments are envisaged to:

i) collect *in-situ* measurements on the more diluted samples (ion-implanted Fe clusters). To this purpose a more compact furnace should be used or the sample chamber has to be modified to avoid the geometric constraints preventing a smaller sample to detector distance

ii) perform *in-situ* high-resolution fluorescence emission measurements to enhance the change observed in the XANES spectrum when the phase transition is inhibited.