ESRF

Experiment title:

Element- and site-selective structural study of iron-iron oxide core-shell nanoparticles by DAFS

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Report:

The goal of experiment HS2027 was to study the local structure in iron-iron oxide core-shell nanoparticles using Diffraction Anomalous Fine Strucutre (DAFS). Element- and site-selectivity are the main features of this technique that allow to separately study the local structure of α-Fe core and spinel oxide shell. Using DAFS we sought to obtain separately information on the local structure around Fe in the core and in the shell, which cannot be gained by using conventional X-ray absorption spectroscopy (XAS) since an average signal is measured.

Iron nanoparticles were synthesized using the IGC technique: 99.98% pure iron was placed into a Joule-heated tungsten crucible and evaporated in presence of 133 Pa of 99.9999% pure He. Nanoparticles are formed by homogeneous nucleation of metallic vapours and convection collects them onto a rotating drum cooled by liquid nitrogen. After restoring high-vacuum conditions (10^{-5} Pa), the passivation procedure is initiated by slowly admitting pure O_2 into the chamber. A pressure of 133 Pa is attained in about one hour. Finally, 1.2 kPa of He are inserted and the nanoparticles are exposed to this atmosphere for 24 hours. The oxidation procedure grows an iron oxide (Fe_yO_x) layer on the metallic cores, producing the core-shell morphology. Oxidized particles (Fe/Fe_yO_x) were then scraped from the collection surface and cold-compacted in form of pellets in high vacuum under an uniaxial pressure of 1.5 GPa.

The mean size of the nanoparticles was controlled by varying the evaporation rate by adjusting the evaporator heating current. The average core diameter was determined with in-house X-ray diffraction; a Philips PW710 diffractometer with Cu-Kα radiation (λ=1.54056 Å) and a graphite monochromator in the diffracted beam were used and the diffraction profiles were analyzed using a Rietveld full profile fitting.

The samples for the DAFS experiment were prepared by depositing the nano-powders on millipore membranes, thus allowing us to change the sample thickness and choose the best absorption/transmission ratio. Millipore membranes were then mounted perpenducularly to the beam, on a specifically designed and built rotating sample holder (~100 rpm).

DAFS measurements were performed in the transmission geometry, with the sample placed perpendicularly to the beam, using the Translating Imaging Plate (TIP) available on GILDA. The TIP consists of a flat Imaging Plate (200(h)x400(v) mm^2) with 100x100 μm^2 pixel size. Two vertical slits select a thin (~3 mm wide in our case) vertical slice of the full diffraction pattern. Several diffraction patterns can be collected translating the Imaging Plate behind the slits. DAFS recording with the TIP consists in exposing one vertical slice of the plate at each monochromator step. At the end of the procedure the TIP reports different diffraction patterns taken at increasing energy tuned around the selected absorption threshold. After image digitization and data treatment procedures a diffractogram for each energy point is obtained. The DAFS signal is extracted from the variation of intensity of the Bragg peaks. The main advantage of TIP method is in collecting wide portion of the diffraction patterns for each energy step allowing for accurately determining the diffraction peak intensity. Moreover this method offers the possibility to extract several DAFS spectra from the same energy scan.

In the figure we report, superposed and arbitrarily normalized, two diffraction patterns taken at 7050 eV (in black) and 7150 eV (in red) (respectively below and above the Fe K absorption edge at 7111 eV) of a sample with core average size of 10 ± 2 nm and a α-Fe volume concentration of 37%; the sharp peaks are due to a small amount of c-Si powders (~5% wt.) included as a standard in the sample. The patterns clearly show diffraction peaks from α-Fe and spinel oxide. The changes in the intensities of the peaks are a manifestation, as expected, of the anomalous scattering effect.

The principal drawback of this set-up is the reduction of the diffraction signal when increasing the beam energy above the absorption edge. This effect is negligible at high energies (>15-20 KeV), but, at the Fe K edge, was found to be very important so that a long exposure was required (more than 40 minutes for each energy point); smaller exposure times lead to unacceptably low statistics and anomalous scattering contrast. Since a DAFS scan must contain at least on the order of 200-300 energy points we unfortunately had to conclude that, at the Fe K edge, DAFS measurements are not feasible in a reasonable time scale using this set up.