



# A XAS study of surface oxidized Fe particles

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## Motivation

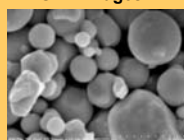
Naturally oxidized, ball milled iron powders exhibit a considerable low field magnetoresistance (MR) at room temperature.

In order to determine the nature of MR effect a XAFS study of the oxides in the outer layers of grains was carried out. Oxygen and iron *K* edge spectra, as well as iron *L*<sub>2,3</sub> edges spectra were measured at room temperature.

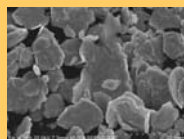
Samples were prepared at the INA, Zaragoza, by ball milling Fe powders for several hours. Some samples were thermally treated at 300 °C in air or vacuum.

Ball milling causes a flattening of the powder particles.

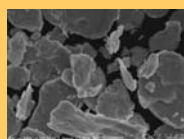
### SEM Images



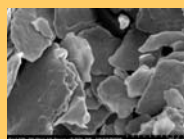
Initial Fe powder before milling



Fe powder after 16h milling



Fe 16h after vacuum annealing



Fe powder after 112h milling

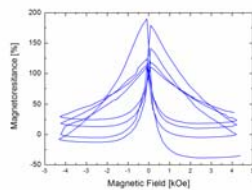


Figure: Example of the magnetoresistivity of the investigated samples, here: the relative magnetoresistance of Fe 16h, measured at INA in Zaragoza, Spain.

## XANES O:K edge

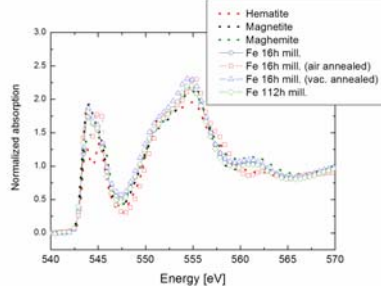
Measurements: BEAR (Bending Magnet for Emission Absorption and Reflectivity) beamline at the Elettra Synchrotron, Trieste. Total electron yield (TEY) detection mode was used.

Data fitted with a linear combination of the reference samples spectra (iron oxides: magnetite Fe<sub>3</sub>O<sub>4</sub>, hematite α-Fe<sub>2</sub>O<sub>3</sub> and maghemite γ-Fe<sub>2</sub>O<sub>3</sub>).

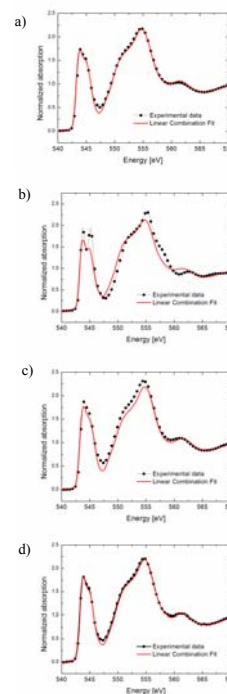
From the fits relative amounts of the oxides were obtained for the layer thickness of 5 nm (photoelectron escape depth at the O:K edge energies).

In all cases except for the air annealed sample magnetite is dominant (with some hematite or maghemite at the outer layer), in the air annealed sample hematite is dominating.

Figure below: XANES oxygen *K*-edge spectra of the samples studied and reference oxides



Figures on the right: XANES oxygen *K*-edge spectra with linear combination fits of the reference oxides spectra. a) Fe 16h milled, b) Fe 16h milled (air annealed), c) Fe 16h milled (vacuum annealed), d) Fe 112h milled



## XANES Fe:L<sub>2,3</sub> edge

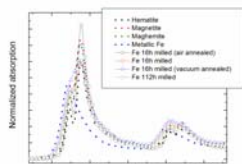


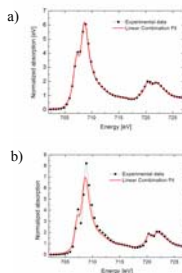
Figure above: XANES Fe *L*<sub>2,3</sub> spectra of the reference oxides, pure iron and some of the samples.

A combination of metallic iron (α-Fe) and combined spectra of reference oxides was fitted. The results confirm the values obtained from the O:K edge analysis.

The approximate oxide layer thickness of 4 nm is determined.

Figures on the right: Examples of the fitted Fe: *L*<sub>2,3</sub> edges XANES spectra:

a) Fe 112h milled, b) Fe 16h milled (air annealed)



## XANES Fe:K edge

The iron *K* edge measurements were performed at the A1 beamline at HASYLAB, Hamburg, in the TEY, TFY and Transmission modes.

For the air annealed sample the linear combination fit of the TEY spectra shows: **38% magnetite, 15% hematite, and 46% α-Fe.**

The other samples show only α-Fe, due to their thin oxide layer of ca. 1% of the electron escape depth for these energies of ca. 300 nm.

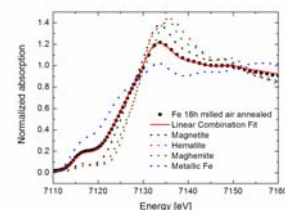


Figure: XANES Fe *K* edge spectra of the reference oxides, α-Fe and the experimental data of the linear combination fit.

## EXAFS O:K edge

Step 1: FEFF simulations for the reference oxides were carried out for the two nearest neighbor shells. Fits provided FEFF parameters for individual oxides.

Step 2: Spectra of milled Fe powders were fitted with the amplitudes determined in the first step by weighing them by the relative amounts of oxides derived from O:K XANES.

The EXAFS fits are in excellent agreement with the XANES data.

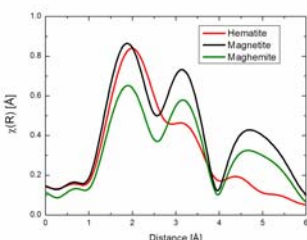
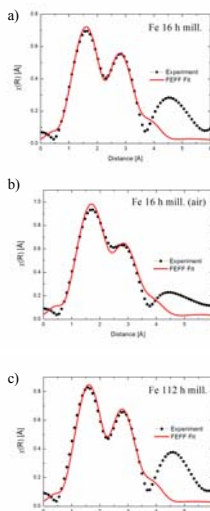


Figure above: EXAFS O:K edge spectra of the reference oxides. Magnetite and maghemite have the same structure (cubic, O<sub>1</sub>-Fd3m), whereas hematite has a hexagonal cell (D<sub>3h</sub>-R-3c). A smaller amplitude for maghemite is due to a lower local symmetry caused by Fe site vacancies. Interatomic distances for the two structures are similar.

Figures on the right: EXAFS spectra fitted with a combination of FEFF path sets. Samples shown in a) and c) show a magnetite-like structure, whereas sample b) a hematite-like structure.

For the fits single and double scattering paths up to ca. 4 Å were used. The first peak is contributed by the nearest Fe neighbors (1.9 – 2.1 Å), the second peak contains signals from the oxygen shell (2.6 – 3.0 Å) and the next Fe shell (3.5 – 3.8 Å)



## Conclusions

For all the samples magnetite (maghemite) is dominant, except for the air annealed sample, (weakest MR response), where the hematite-like oxide is dominant.

The air annealed sample has the oxide layer of approximately 200 nm thickness, whereas for the other samples it is of 3 – 5 nm.

The outermost oxide layer is hematite or maghemite-like. The sample (vacuum annealed) exhibiting a maghemite-like outer layer shows the highest MR response.

Table: The relative oxygen amounts determined from XANES O:K edge spectra.

	Magnetite	Hematite	Maghemite
Fe 16h	0.606	0.116	0.278
Fe 16h (air)	0.401	0.599	0.000
Fe 16h (vacuum)	0.645	0.000	0.355
Fe 112h	0.841	0.171	0.000
Fe 336h	0.561	0.130	0.310
Fe 1h	0.276	0.124	0.600

Note: the numbers do not sum up to 1 due to the fact that they were determined with uncertainties.

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