EXAFS study of iron nanoparticles with oxide shell

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ABSTRACT

Purpose: The aim of this work is to present the results of the study of the local structure of iron nanoparticles with oxide shell which uses EXAFS method that apply synchrotronic radiation.

Design/methodology/approach: The samples used in the carried out analysis were as follows: pure iron powder, pure iron powder containing nanoparticles and pure iron powder containing nanoparticles subjected to 224 hours of grinding.

Findings: The local structure of iron nanoparticles with oxide shell were found.

Research limitations/implications: It was not enough time to measure O:K edge.

Practical implications: The analysis of spectra does not reveal any iron oxides in samples. More accurate results would be obtained at oxygen K edge.

Originality/value: It was proved that iron nanoparticles with oxide shell samples had the local structure characteristic for metallic iron.

Keywords: Nanomaterials; Magnetite; EXAFS

MATERIALS

1. Introduction

The iron nanoparticles with surface oxides exhibit very unique physical properties. One of them is the giant magneto-resistance (GMR). This effect is strongly influenced by the existence of the oxide layer. The GMR effect was observed in the 1980s in thin magnetic layers separated by nonmagnetic layers. This effect consist of a huge changes in the electrical resistivity in weak magnetic fields. GMR is already used by the industry on a large scale. In mass produced devices the change in the resistivity reaches up to $R/R_0 \approx 40\%$ [3]. In devices produced in former times the maximum values of $R/R_0 \approx 2\%$ were reached (permalloy). These new materials are to be used potentially e.g. in the data storage technology.

2. Description of the approach

XAS (EXAFS and XANES) is a spectroscopic technique that uses X-rays to probe the physical and chemical structure of matter at an atomic scale. XAS is element-specific, in that X-rays are chosen to be at and above the binding energy of a particular core electronic level of a particular atomic species. Because all but the lightest elements have core-level binding energies in the X-ray regime, nearly all elements can be studied with XAS. The emphasis has traditionally been on the heavier elements (of Z>15 or so).

The aim of this work is to present the results of the study of the local structure of iron nanoparticles with oxide with use of computer simulation of the local structure.

EXAFS method is based on the curved dependency of the absorption ratio against energy radiation. The EXAFS was used to find the localization of the atoms in the nanoparticles' structure. The samples used for the analysis performed were as follows: pure iron powder, pure iron powder containing nanoparticles and pure iron powder containing nanoparticles subjected to 224 hours of grinding. The spectra at the Fe:K edges were analysed. The iron nanoparticles with oxide shell consists of a core (α - iron) and a thin layer of iron oxides (of a

few nanometres in height). They possess unique physical qualities such as the giant magnetoresistance effect (GMR).
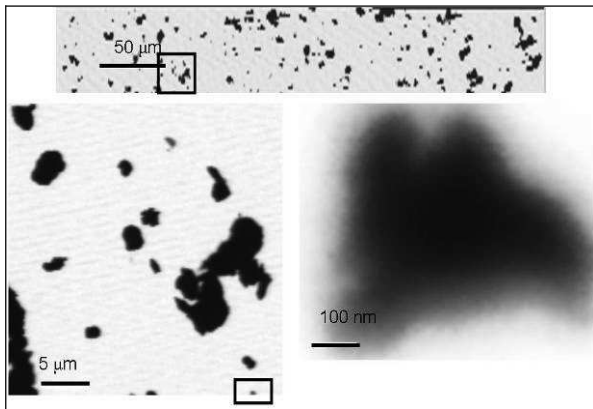

Fig. 1. Pure iron powder containing nanoparticles Fe 224h.

3. Description of achieved results of own researches

EXAFS data analyse indicate that samples Fe 0h and Fe 224h have atomic structure similar to iron metallic structure. The radial distribution functions for iron metallic and for the both Fe 0h and Fe 224h samples are the same. Ibarra et al. says, that theoretically nanoparticles should have oxide coating layer about 2 – 5 nm [9].
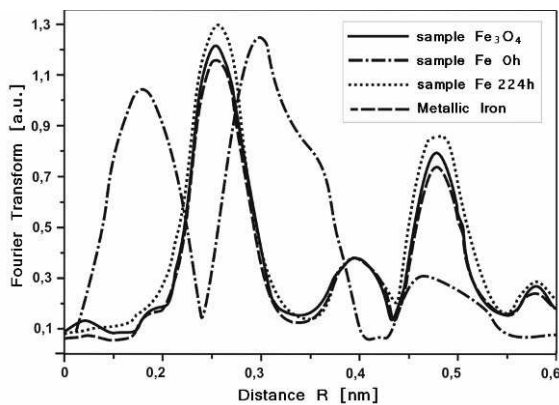

Fig. 2. Fourier Transform for metallic iron, Fe_3O_4 sample (clean magnetite), Fe 0h sample and Fe 224h sample.

Data analysis also exhibits that there is no oxide surface layer on iron nanoparticles. The atomic structure of Fe 0h and Fe 224h is the same as for metallic iron (Fig. 1).

In the radial distribution function for magnetite Fe_3O_4 (Fig. 2) one could observe a peak in 0,19 nm which corresponds to oxygen. In case of presence of oxygen atoms the same peak at the same distance should be observed for Fe 0h and Fe 224h samples. One can suppose, that the absence of this peak is caused by too

deep penetration (of the order of micrometers) of hard X-ray into experimental sample. The atoms from deeper areas of sample were excited. EXAFS measurement at oxygen K edge should confirm the presence of oxide surface layer in Fe 0h and Fe 224h sample .EXAFS data analysis was used to determine local atomic structure of Fe 0h and Fe 224h samples and to compare with metallic iron structure. The theoretical and experimental EXAFS spectrum was fitting. Shape of absorption edge was calculated using IFFEFIT package.

In order to compare the experiment with theory the EXAFS spectrum for ideal structure alpha-Fe was simulated using Artemis program from IFFEFIT package (Figs. 3-12). The spectrum received was fitting to experimental data for Fe 0h and Fe 224h samples. Both curves are identical. That confirms the assumption, that samples have atomic structure the same as metallic iron.
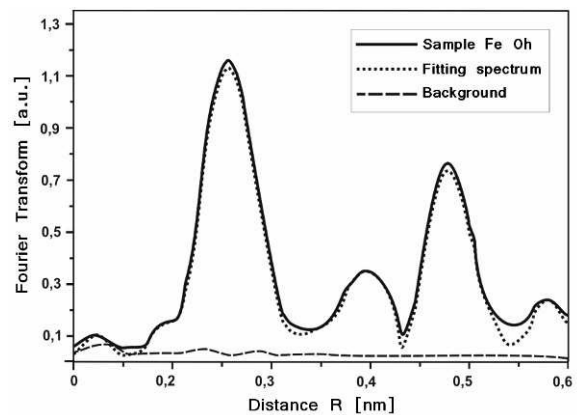

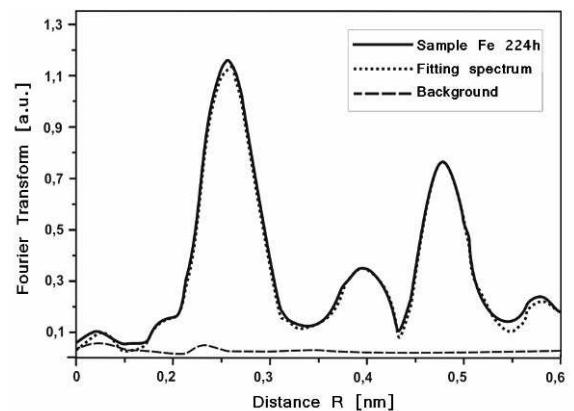Fig. 3. Fitting of theoretical to experimental spectrum for Fe 0h sample (fitting space 0 – 0,60 nm).

Fig. 4. Fitting of theoretical to experimental spectrum for Fe 224h sample (fitting space 0 – 0,60 nm).

At the same time, on the basis of the results obtained, it was found that the central atom is surrounded by 8 iron atoms in 0,247 nm and 6 atoms of iron in 0,285 nm (first peak), 12 iron atoms in 0,405 nm (second peak), 24 atoms in 0,475 nm (third peak).