Properties of iron nanoparticles sealed in protective media

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Abstract. Iron nanocrystalline powder was prepared by the reduction of ferrihydrite. The samples were sealed in Ar in a plastic bag to avoid any contact with air in the form of (i) the as-prepared powder, (ii) the powder mixed with a vacuum grease, and (iii) the powder after a very slow oxidation at room temperature which formed an oxidic shell. Their phase compositions were investigated by XRD and Mössbauer spectroscopy. These data were completed by magnetic measurements. The intense amorphous-like component was observed in the Mössbauer spectrum of the as-prepared powder. The origin of this component is discussed.

1. Introduction
The strong affinity of iron nanoparticles to oxygen causes that most samples of this material after handling in the air are formed by iron cores with oxidized shells or fully oxidized. To prevent oxidation of iron nanoparticles protective shells must be prepared before the contact with ambient atmosphere or they must be kept in a protective medium immediately after the preparation, e.g., in high vacuum, stable liquids, gels or atmospheres. Most of the studies of iron nanoparticles were carried out on the samples of iron particles with protective shells. Therefore an investigation of the as-prepared bare nanoparticles would show new information on the phase composition, magnetic behaviour, dynamics, etc.

Various problems of dynamics of nanoparticles were often discussed, e.g., in [1] and the references therein. The nanoparticles were attached to the macromolecules and their dynamics was monitored in [1]. The samples of iron-carbon nanoparticles in hexadecane and decaline using oleic acid as a surfactant were investigated. The broad component in the Mössbauer spectrum in decaline whose temperature was slightly below melting point was interpreted to be due to Brownian oscillations. The broad component was not observed in a sample where the nanoparticles were in hexadecane. This very important difference was explained by the properties of the organic material in the immediate vicinity of the particles which determine their motion.

Recently Stanek et al. [2–4] used Mössbauer spectroscopy as a tool for the determination of the microscopic movements of nanoparticles in various media. They mixed 100 nm hematite particles in various substances such as soft gels, foams, sugar solution, etc., and measured Mössbauer spectra of these samples. By the analysis of the resonance absorption line shape in these spectra they obtained that the particles exhibit mobility in the range of mm/s. For the particles in solution of sugar they concluded that the particle movement is correlated for an interparticle distance less then 300 nm.

In this work we will show a different model of the analysis of the spectra of iron nanoparticles which are sealed in protective media. For this purpose we are using comparison of the three types of iron nanoparticles of the same size distribution but with some differences in the phase composition.

2. Experimental details
The nanocrystalline iron powder was prepared by the reduction of ferrihydrite in hydrogen atmosphere at 620 °C for 18 hrs and slowly cooled down (2 K/min) to room temperature. Subsequently the as-prepared powder
was packed in PVC plastic bags or in Cu containers in Ar atmosphere without a contact to ambient air (sample labelled A). The samples of the powder closed in plastic bags were used for XRD and Mössbauer measurements and the powders in Cu containers for magnetic measurements. The powder for the sample B was mixed with a vacuum grease and sealed in the same way as the sample A. The slowly oxidized powder sample (labelled C) was prepared by pumping out the furnace atmosphere after calcination followed by a pressure increase from $10^{-2}$ to $10$ Pa during four days. This slowly oxidized powder was no more pyrophoric by a contact with the ambient atmosphere. It was nevertheless sealed in a plastic bag with Ar as was done in the case of the sample A.

The structure and phase composition of the powder were investigated by an X-ray diffraction and Mössbauer spectroscopy. The X-ray powder diffraction patterns were collected using CoK$_\alpha$ radiation. The $^{57}$Fe Mössbauer spectra were measured in transmission geometry using $^{57}$Co(Rh) source. The velocity calibration was done according to a pure $\alpha$-Fe foil. The line width of the sextet of the calibration $\alpha$-Fe foil was 0.25 mm/s and 0.29 mm/s at 293 K and 5 K, respectively. The Mössbauer absorber was formed by the powders which were sealed in plastic bags in-situ and covered by the additional Al foil for better temperature homogeneity inside the absorber. The absorbers were placed in the cryostat sample holders. The thickness of the absorbers corresponded to ~ 9 nm Fe foil. The morphology and size of the powder particles C were checked using TEM. The magnetic properties were measured using a vibrating sample magnetometer: the hysteresis loops in external field up to ±10 kOe and the temperature dependence of the magnetic moment in 100 Oe.

3. Results and discussion

The X-ray results (Fig. 1) show that the samples of the powder held in Ar in plastic boxes contained bcc Fe with the mean coherence length ~ 10 nm calculated using Scherrer formula. The diffraction data of the sample C show fine peaks of iron oxides. Their content according to a phase analysis was lower than 5 wt.%. TEM of the powder in the sample C shows core-shell particles with a mean size about 25 nm.

The hysteresis loop of the sample A indicated weakly interacting ferromagnetic particles with coercivity 40±4 Oe. The loop of the sample C was very similar with a slightly decreasing magnetic moment and increasing coercivity to 190±10 Oe. Both changes can be simply ascribed to the presence of the oxide phases. The decrease in the magnetic moment roughly corresponds to the oxidation ~ 10 % of iron atoms. The temperature dependence of the magnetic moment of the sample A indicated, that Hopkinson effect starts at ~ 870 K. No changes can be observed below this temperature which indicates stability of the sample.

![Figure 1 XRD of the sample A (top) and sample C (bottom).](image)

The Mössbauer spectrum of the sample A at room temperature (Fig. 2) can be divided into two main components. The first one corresponds well to $\alpha$-Fe with the same parameters as the bulk bcc iron. The
second component – amorphous-like - must be fitted by three sextets with hyperfine field distribution. The value of the mean hyperfine field $<B_{hf}>$ of these components is $33.2 \pm 0.3$ T, i.e. very close to $\alpha$-Fe, but the mean isomer shift is $+0.09 \pm 0.03$ mm/s. The $\alpha$-Fe sextet dominates in the spectrum of the sample B. In addition a weak broad sextet on the background and the doublet with isomer shift $0.36 \pm 0.05$ mm/s representing Fe$^{3+}$ can be analyzed there. The spectrum of the sample C is clearly composed of the sextet of $\alpha$-Fe and by a doublet with an isomer shift and quadrupole splitting corresponding to Fe$^{3+}$.

By temperature decrease down to 5 K the spectrum of the sample A changes to a broad sextet with hyperfine parameters of $\alpha$-Fe. It is possible to fit the spectrum by one $\alpha$-Fe sextet (at 5 K) and three sextets as at room temperature spectrum but the hyperfine field distributions are substantially narrower. In the spectrum of the sample B the broad sextet on the background diminishes at 5 K. For the sample C, the doublet in the room temperature spectrum transforms to a sextet which represents Fe$^{3+}$ oxides. It should be noted that the intensity ratios inside the sextets were kept at 3:2:1, i.e. random distribution of spin orientations, was expected for all samples in the fitting procedure used.

Superparamagnetic component was not observed in the spectra of all the samples. It can be an influence of the exchange interaction which suppresses superparamagnetic relaxation. It was found in agglomerated NiO nanoparticles [5] and in composites containing antiferromagnetic nanoparticles of different materials [6]. The shape of the room temperature spectrum of the sample A is very similar to some of that shown in [2,3]. However there is an objection against explanation of the present results in frame of Brownian motion model. The sample C does not exhibit the same broad sextet components as the sample A although both samples are very similar from the point of view of the particle sizes. Diffusion (even in surfaces) may be excluded because the component (in a narrower form) remains in the spectrum taken at 5 K where the atomic jumps have a negligible probability. Structural disorder in the surface layer could be another cause of the broad component in the 295 K spectrum of the sample A. The mean size of the particles was $\sim 20$ nm. The atomic fraction of the amorphous-like component was of 0.77. It corresponds to the mean thickness of a surface layer $\sim 4$nm. The structural disorder could be removed (ordered) by the slow oxidation (sample C). However it is less probable that such a disorder can be removed (ordered) by mixing of the nanopowder with a vacuum grease. The only difference is in their surface. In the sample A the particles have a “raw” iron surface while in the sample C the surface is formed by a Fe$^{3+}$ oxide shell.
Table 1. The results of the analysis of the Mössbauer spectra shown in figs. 4 and 5 (S ... sextet, D ... doublet, intensities I of the components in atomic fraction of Fe atoms – a.f., hyperfine inductions $B_{hf}$, $\Delta B_{hf}$ width of distribution of $B_{hf}$, isomer shifts $\delta$, quadrupole shifts $\varepsilon_Q$, and quadrupole splittings $\Delta\varepsilon_Q$).

| Sample | T [K] | Component | I [a.f.] | $B_{hf}$ [T] | $\Delta B_{hf}$ [T] | $\delta$ [mm/s] | $\varepsilon_Q$ [mm/s] | $\Delta\varepsilon_Q$ [mm/s] |
|--------|-------|-----------|---------|-------------|----------------|---------------|----------------|----------------|
| A 293  | S1    | 0.21      | 33.1    | -           | 0.03           | 0.01          | -              | -              |
|        | S2    | 0.27      | 36.9    | 3.1         | 0.56           | -0.44         | -              | -              |
|        | S3    | 0.24      | 34.8    | 2.3         | -0.27          | 0.44          | -              | -              |
|        | S4    | 0.27      | 31.5    | 1.3         | 0.12           | -0.14         | -              | -              |
|        | D1    | 0.01      | -       | -           | 0.46           | -             | 1.08           | -              |
| 5      | S1    | 0.21      | 34.2    | -           | 0.15           | 0.02          | -              | -              |
|        | S2    | 0.57      | 34.0    | 0.6         | 0.25           | -0.01         | -              | -              |
|        | S3    | 0.22      | 33.1    | 2.9         | 0.65           | -0.73         | -              | -              |
| B 293  | S1    | 0.64      | 33.0    | -           | 0.00           | 0.00          | -              | -              |
|        | S2    | 0.33      | 32.5    | 1.3         | 0.12           | 0.30          | -              | -              |
|        | D1    | 0.03      | -       | -           | 0.14           | -             | 0.68           | -              |
| 5      | S1    | 0.95      | 34.2    | -           | 0.15           | 0.03          | -              | -              |
|        | S2    | 0.03      | 32.5    | -           | 0.89           | -0.32         | -              | -              |
|        | D1    | 0.02      | -       | -           | 0.16           | -             | 1.00           | -              |
| C 293  | S1    | 0.86      | 32.9    | -           | 0.03           | 0.00          | -              | -              |
|        | D1    | 0.14      | -       | -           | 0.37           | -             | 1.43           | -              |
| 5      | S1    | 0.87      | 34.2    | -           | 0.15           | 0.00          | -              | -              |
|        | S2    | 0.13      | 48.8    | 0.9         | 0.56           | -0.17         | -              | -              |

There acts another source which is responsible for the surface component having amorphous-like subspectrum in the sample A. The high volume content of the interfaces/surfaces is taken as the most important feature of nanocrystalline metals and oxides since the beginning of their studies. It can be expected that the atoms in a surface layer can be influenced by changes in the electron densities which do not “freeze” contrary of phonons at 5 K and therefore changes in hyperfine field parameters can be expected in the whole temperature range.

Acknowledgements
This work has been supported by the project 1M619895201 of the Ministry of Education of the Czech Republic and by the Grant Agency of the Czech Republic (106/08/1440).

References
[1] Hendriksen P V, Mørup S and Linderoth S 1992 Hyperfine Interaction 70 1079
[2] Stanek J and Fornal P 2009 Hyperfine Interactions DOI 10.1007/s10751-009-9967-y
[3] Fornal P and Stanek J 2008 Acta Phys. Polonica A 114 1667
[4] Fornal P, Stanek J and Wilk A 2008 Hyperfine Interactions 185 81
[5] Bodker F, Hansen M F, Koch C B and Mørup S 2000 J. Magn. Magn. Mater. 221 32
[6] Frandsen C and Mørup S 2003 J. Magn. Magn. Mater. 266 36