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Mössbauer study of magnetite nanowire in MCM-41 type mesoporous silica templates

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Abstract. Arrays of Fe_3O_4 nanowires embedded in mesoporous ordered silica were obtained in two ways: dissolving Fe^{3+} ions in an aqueous medium and their adsorption on internal and external surfaces, with the use of a Fe-EDTA complex. Magnetite polycrystalline nanowires were characterized by means of X-ray diffraction and ^{57}Fe Mössbauer spectroscopy (MS). The average length of these nanowires is about 70 nm and their diameter is about 3 nm. Mössbauer studies evidenced that the composites consist of very small Fe_3O_4 particles. Almost 80% of particles exist in a paramagnetic state.

Key words: hyperfine interactions • Mössbauer effect • MCM-41 silica • nanowires

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Introduction

During the last few years, nanowires have attracted much attention due to their importance for fundamental studies and the wide range of potential applications in nanodevices. Nowadays, there is a lot of methods to fabricate nanomaterials, particularly, such as one-dimensional or quasi-one-dimensional nanostructures. For example, by electron-beam lithography (EBL) [4] or nano-imprint lithography one can produce characteristic features of the order of 25 nm. Preparation and magnetic properties of nanowire arrays in the anodic aluminum oxide (AAO) templates have been recently intensively explored [7, 8, 10]. Other alternative methods are using mesoporous ordered silica materials.

The M41S mesoporous ordered silica materials were invented in 1992 by the Mobil Oil group [2]. One of such materials, which is characterized by a uniform pore diameter, large pore volume and large surface area, is MCM-41. The hexagonal arrangement of the cylindrical pores is obtained in MCM-41 by the use of templating technique. Cylindrical micelles created by a surfactant in an alkaline medium are used as condensation centres for silica from tetraethylorthosilicate (TEOS), or alkalimetal silicate. Accumulation of micellar rods leads to creation of honeycomb shaped micelle-templated silica. Using the templates with an alkyl chain of a varying length, allows controlling pore diameters in the range of 2 to 10 nm. Pyrolysis at 820 K is one of the standard procedures for a template removal.

The analogous sample MCM-41(C18TAB) was studied using the positron annihilation method and nitrogen adsorption/desorption technique to obtain nanosize of pores. The pores of radii 1.5 ± 0.2 nm and 1.52 nm have been determined by means of the pick-off technique and liquid nitrogen (LN) sorption, respectively [2, 9].

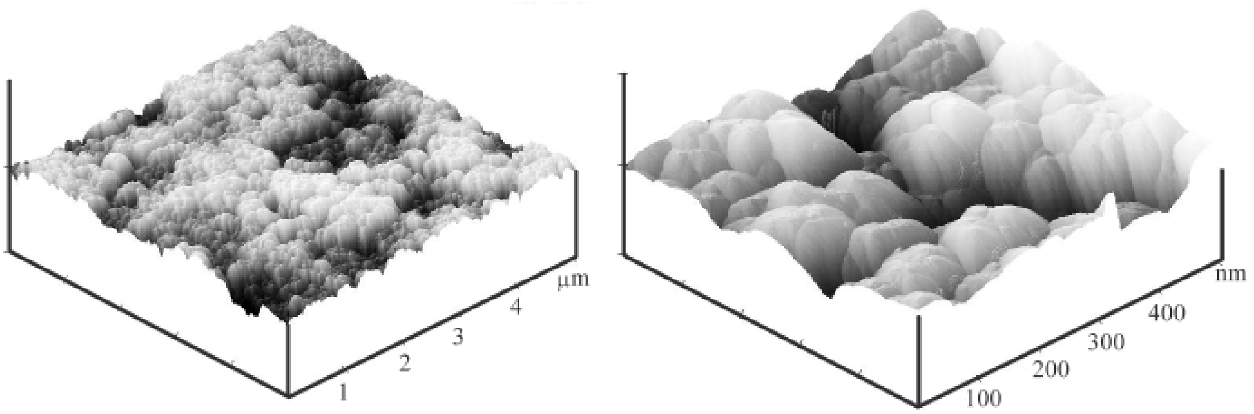

Fig. 1. The AFM images of the surface of investigated particles MCM-41 for a different zoom.

In this work, the magnetite nanowires arrays with a 3.0 nm diameter put in the MCM-41 type mesoporous silica templates were prepared in two ways. Magnetic properties at different temperatures were investigated with a particular account of the finite-size effects.

Experimental

MCM-41 materials were prepared [1] using octadecyltrimethyl ammonium bromide (C18TAB) as a template and TEOS as a silica source. The mixture was annealed at 323 K for 10 h. The pH value was adjusted to 11.0. The synthesis process lasted an hour while the solution was stirred. The solids thus prepared were calcined from room temperature up to 300°C for 2 h under air flow and then at 550°C for 4 h in order to remove the surfactant. In the second step the calcined samples were impregnated in two ways:

(i) by inserting 5% solution of Fe^{3+} into porous silicate for 0.5 h, drying (1 h) and calcination in air atmosphere at 110°C for 1 h,

(ii) by washing with 0.1 molar Fe-EDTA (ethylenediaminetetraacetic acid) solution for 0.5 h and drying at 110°C for 1 h. Then, the samples were put into 5% aqueous Fe^{3+} solution and the next stage was the same as above in (i).

The structure of grain crystallite MCM-41 was obtained by means of an atomic force microscope (AFM). Phase analysis of impregnated magnetite nanowires was carried out by means of X-ray powder diffraction (XRD) with CuK_α radiation. The scans were obtained in the range from 25° to 60° (2θ). The Mössbauer spectra of powder samples were recorded using a constant acceleration spectrometer in the temperature range 300–900 K with a $^{57}Co(Rh)$ source. The Mössbauer spectra were fitted using the least-squares procedure, where the quadrupole interaction was treated as a perturbation to the hyperfine field. The isomer shift (IS) values are given with respect to α-Fe at room temperature.

Results and discussion

The images of surface of particles obtained by means of AFM are presented in Fig. 1. The grains and crystallites built of these grains can be seen. The analysis of these images allows to estimate the average size of grains which is found to be 70(5) nm. It can be assumed that the length of nanowires is comparable with the size of crystallite. The limited resolution of AFM does not allow to observe the porous structure of MCM-41 type silica.

The X-ray diffraction patterns of Fe_3O_4 nanowires in the MCM-41 silicate template are shown in Fig. 2. The lowest pattern (a) corresponds to the sample prepared by inserting in the solution of Fe^{3+} (sample 1). Fe-EDTA complex + solution of Fe^{3+} (sample 2) is shown in (b). For a comparison, the bulk magnetite pattern is shown in (c). The lattice parameters *a* of Fe_3O_4 crystalline nanowires structure are 8.341 Å and 8.339 Å for samples 1 and 2, respectively. These

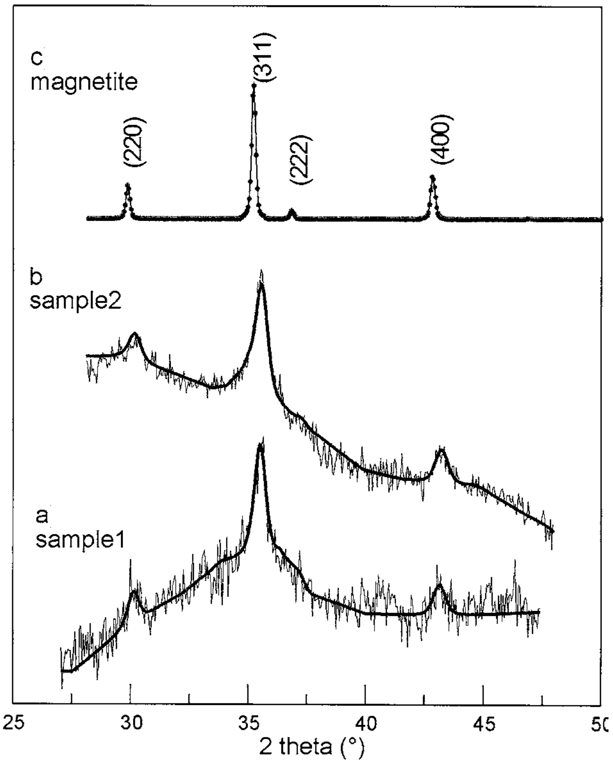

Fig. 2. The XRD diffraction patterns of Fe_3O_4 nanowires in the MCM-41 silicate template (a, b) and diffraction patterns of well crystallized Fe_3O_4 (c).

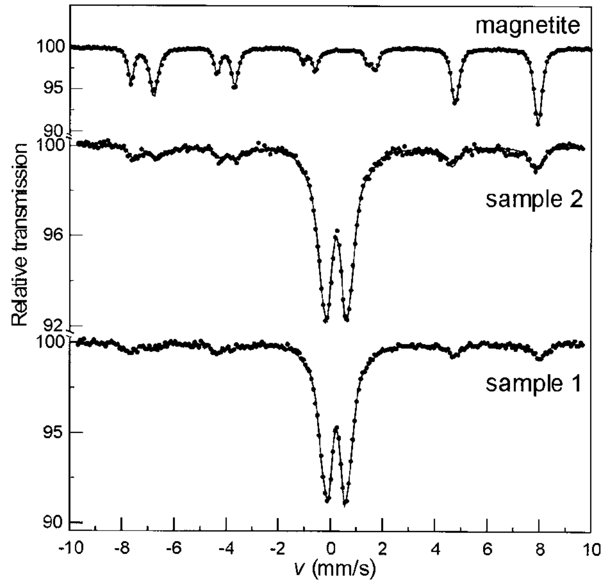

Fig. 3. The ^{57}Fe Mössbauer spectra for Fe_3O_4 nanowires at RT in the MCM-41 silicate template.

parameters are slightly smaller than those of the bulk material (a = 8.396 Å). The average grain size: 13.0(5) nm and 11.1(5) nm were deduced from a broadening of the XRD diffraction peaks using the Sherrer's formula.

Figure 3 shows the Mössbauer spectra of magnetite nanowires in the MCM-41 type silicate templates at room temperature for different ways of matrix impregnation. Both patterns consist of two subspectra of a sextet and a superimposed paramagnetic doublet. The line broadening of the sextets and the doublet suggests that there is a distribution of hyperfine parameters which is due to the size distribution of crystallites.

The paramagnetic doublet results from the relaxation phenomenon due to the intrinsic finite-size effect. The intensity ratio of the sextet peaks is about 3:2:1, indicating that the nanowires in the MCM-41 template are randomly oriented in space.

The occupation ratio of the cations in A and B sites is distinct for different processes of nanowires preparation. In the first case (without Fe-EDTA complex), the occupation ratio is 2:1, in the second case (with Fe-EDTA complex) it is 1:1. However, in the bulk the ratio is 1:2. This effect was observed in nanowires arrays at anodizing anodic alumina oxide [6]. The Fe^{2+}/Fe^{3+} ratio was determined by using the relative areas of the elementary patterns representing the microenvironments of $Fe^{2+}$and Fe^{3+}.

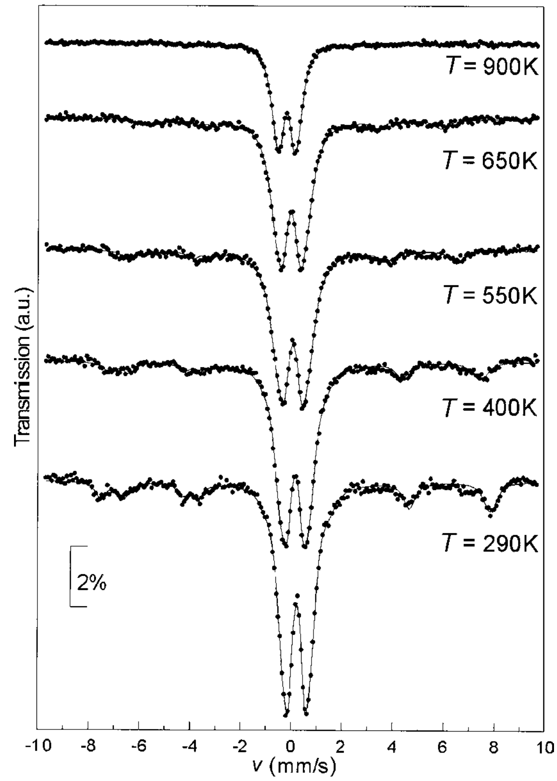

Fig. 4. The ^{57}Fe Mössbauer spectra of Fe_3O_4 nanowires (sample 2) at various temperatures.

The hyperfine interaction parameters for the ferrimagnetic contributions and the superparamagnetic component at room temperature for Fe_3O_4 nanowires and bulk material are collected in Table 1. The hyperfine magnetic field values at RT are similar or slightly smaller than in the well crystallized magnetite. However, the half-width at half-maximum (HWHM) is clearly larger. Such a set of parameters indicates that the superparamagnetism phenomena occur in the investigated samples. The superparamagnetism is also reflected in the Mössbauer temperature measurements. Increase of the paramagnetic phase contribution relative to the magnetic ones with an increasing temperature from 76(2)% at RT to 93(3)% at 650 K and from 80(2)% at RT to 95(3)% at 750 K for sample 1 and sample 2, respectively, was observed in the series of Mössbauer pattern (Fig. 4).

Table 1. The Mössbauer parameters of Fe_3O_4 nanowires in the MCM-41 silicate template and bulk material at room temperature

		Relative intensity (%)	Linewidth FWHM (mm/s)	Isomer shift (mm/s)	Quadrupole shift (mm/s)	Hyperfine magnetic field (T)
Sample 1	Fe^{3+} (tet.)	63(5)	0.25(2)	+0.28(3)	0.02(7)	49.0(5)
	Fe^{2+} (oct.)	36(5)	0.28(3)	+0.60(3)	–0.07(7)	45.7(5)
Sample 2	Fe^{3+} (tet.)	48(5)	0.24(3)	+0.29(3)	0.04(7)	48.2(5)
	Fe^{2+} (oct.)	52(5)	0.28(3)	+0.61(3)	–0.03(7)	44.7(5)
Bulk	Fe^{3+} (tet.)	33.2(2)	0.12(1)	+0.26(1)	0.012(2)	49.1(1)
	Fe^{2+} (oct.)	66.8(2)	0.16(1)	+0.64(1)	0.002(1)	46.0(1)

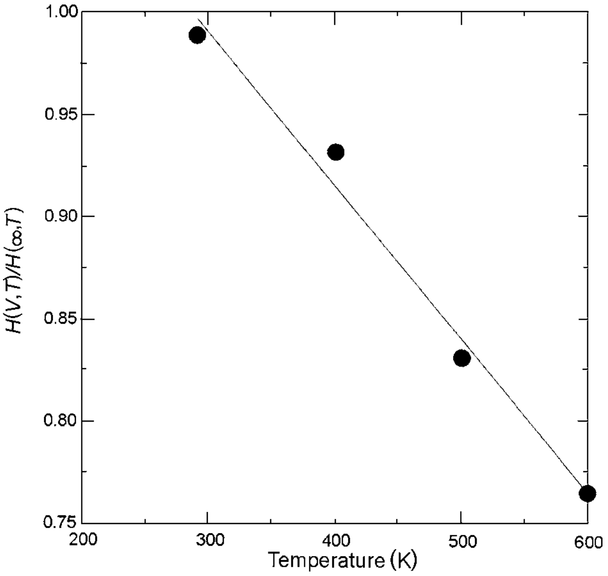

Fig. 5. The normalized hyperfine magnetic field values for the sample 1 vs. temperature.

The critical temperature is lower than that in the case of the well crystallized magnetite because of magnetic domain relaxation. For small size particles, there is a critical temperature called the blocking temperature (T_B) below which the magnetic moments are fixed, i.e. their approach to thermodynamic equilibrium is blocked.

For a particle of volume V, the hyperfine magnetic field at temperature T is expressed as [3]:

$$H(V,T) = H(\infty,T)(1 - kT/2KV) \tag{1}$$

where $H(V,T)$ is the hyperfine field, $H(\infty,T)$ is the magnetic hyperfine field in the absence of magnetic fluctuations, k is the Boltzmann's constant and K is the magnetic anisotropy energy constant. A linear decrease of the hyperfine field vs. temperature in the range 290–600 K is shown in Fig. 5. The value of $H(\infty$,T) was derived from the bulk material. For the size of 3.04 nm in diameter and 13 nm length obtained from the nitrogen adsorption/desorption isotherms and the XRD results, the anisotropy energy value determined from the slope of the best-fitted linear dependence is about $K = 0.91*10^5$ J/m^3.

Summary

The results presented in this paper show that the iron oxide nanowires, in particular magnetite nanowires, could be successfully fabricated in the MCM-41 type mesoporous silica templates. Mössbauer spectroscopy is a very useful tool to study magnetic properties, local electric field and phase structure in nanosized crystallites. Major part of Fe_3O_4 exists in the superparamagnetic state. The contribution of the paramagnetic phase increases with increasing sample temperature. A different way of impregnation of the pores leads to an inconsiderable change of HMF and to different occupation ratios of tetrahedral and octahedral positions occupied by Fe^{2+} and Fe^{3+} cations. The values of quadrupole splitting in nanowires are large because of a large ratio of the number of ^{57}Fe probes located on the surface to that of ^{57}Fe probes located in the volume. The local surroundings on the surface have a reduced symmetry which is related to a large electric field gradient at the iron nuclei.

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