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Mössbauer and magnetic studies of nanocomposites containing iron oxides and humic acids

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Abstract Nanocomposites containing iron oxides and humic acids were studied by Mössbauer and magnetic measurements. The concentrations of humic acids as the precursor in nanocomposites were varied. Mössbauer investigations were carried out at temperature range from room temperature to 5 K. The magnetization *M(T, H)* was measured in the temperature interval 80–300 K and magnetic field up to 10 kOe. It was found that particles of investigated nanocomposites exhibit superparamagnetic properties. The core of the nanocomposite was a mixture of non-stoichiometric magnetite and maghemite. The "iron-polymer" interface was formed on the surface of the iron oxide particles.

Keywords Mössbauer spectrometry · Nanocomposite · Nanoparticles · Humic acids

1 Introduction

The use of nanoparticles covers virtually all areas of technology. The widespread use of nanoparticles is due to the appearance of their new properties. Recently, researchers are showing a greater interest in the study of nanoparticles of iron oxides associated with natural polymeric compounds. Such complexes, known as nanocomposites, have not only ferromagnetic properties but also natures of organic compounds, which are non-toxic and biocompatible and thus suitable for use in biology and medicine. Preparation of nanoparticles of iron oxides in the presence of polymers provides available way to create unique nanocomposite materials which can be used in magnetic separation technique, in the technologies of medical, material science, and pharmaceutical chemistry. Nanocomposites

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prepared by binding the iron oxide and humic acids are effective for solving environmental problems.

2 Objects and methods

Nanocomposites were prepared using Fe_3O_4 nanoparticles and humic acids (HA) with in situ chemical precipitation method [1]. The magnetic Fe_3O_4 particles were prepared from Fe(II) and Fe(III) salt solutions by addtion of NH_4OH [1]. The concentrations of HA as the precursor in nanocomposites were varied.

Mössbauer investigations of nanocomposites were carried out at temperature range from room temperature to 5 K. The isomer shift was given by relative α-Fe. Mössbauer spectra were processed by the program SpectrRelax [2].

The magnetization $M(T, H)$ was measured for some samples in the temperature interval 80–300 K and magnetic field up to 10 kOe. ZFC and FC measurements of $M(T)$ and measurements of hysteresis loops were also performed.

3 Mössbauer study

The room temperature Mössbauer spectra of the nanocomposites based on iron oxide (Fe_3O_4) and humic acids (HA) prepared by chemical precipitation method are typical of superparamagnetic particles (Fig. 1). Spectra were fitted by one doublet and extracting the hyperfine magnetic field distribution in the frame of many-state superparamagnetic relaxation model [3].

The appearance of the quadrupole doublet with average value of isomer shift $\bar{\delta} = 0.35$ mm/s and quadrupole splitting $\bar{\Delta} = 0.72$ mm/s that show typical positions of the ferric atoms in the octahedral environment of oxygen atoms is likely to be associated with the formation of a new phase on the surface of the nanocomposite, or due to the superparamagnetic relaxation. The doublet relative intensity increases with increasing the concentration of humic acids like the precursors of the nanocomposite.

The parameter $\alpha = K_{\mathrm{eff}}V/kT$ (K_{eff}—the effective anisotropy energy constant, V–the particle volume, k–Boltzmann's constant, T–the temperature), which is used for spectra processing by many-state superparamagnetic relaxation model decreased with the increase in the concentration of humic acids like precursors in nanocomposites. This dependence indicated a reduction of the nanocomposite particle sizes.

Mössbauer spectra of the samples were measured at 5 K (Fig. 2) to avoid the relaxation processes and to identify the phases more precisely. Spectra were processed by using the model consisting of three Zeeman sextets and one quadrupole doublet. First sextet corresponds to the positions of Fe^{3+} atoms in octahedral environment of oxygen, the second one, to Fe^{3+} atoms in tetrahedral positions, the third one, to Fe^{2+} atoms in octahedral environment.

The analysis of the spectrum of the sample with 0 % HA (sample without addition of humic acids) have shown that the initial substance is a mixture of magnetite Fe_3O_4 and maghemite y-Fe_2O_3 rather than pure magnetite. The quadrupole doublet was not observed for this spectrum. However the doublet with extended lines is even observed in Mössbauer spectra at the concentration of 20 % HA. Therefore the appearance of this doublet could be explained by the formation of the “iron-polymer” interface in nanocomposite caused by the interaction between the surface of the iron oxide nanoparticle and the macromolecules of

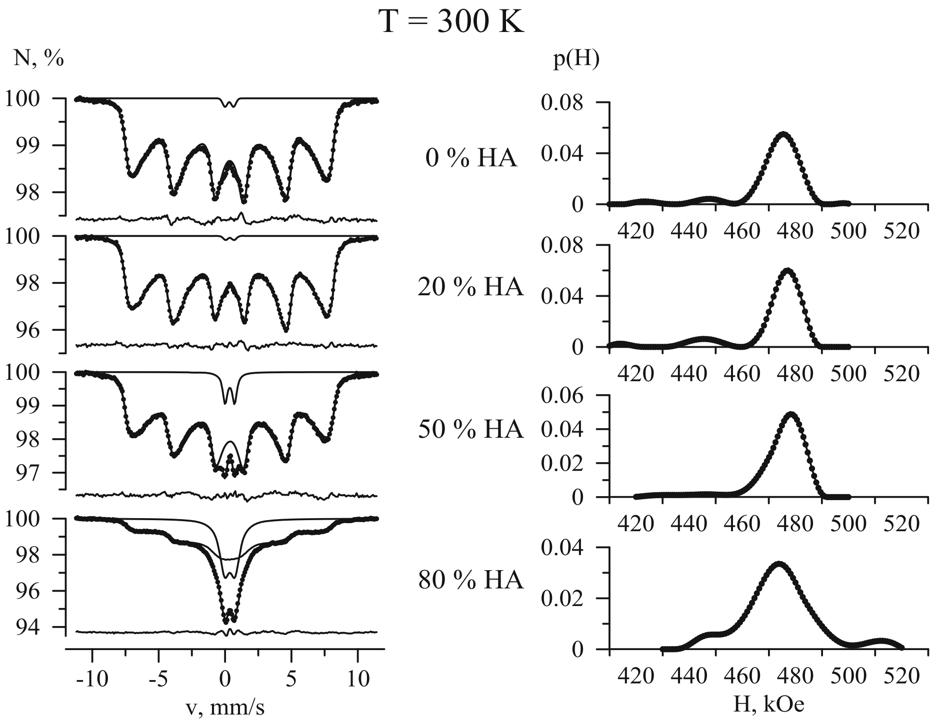


Fig. 1 Mössbauer spectra of the nanocomposite samples with different concentration of humic acids measured at room temperature and corresponding distributions of hyperfine magnetic field $p(H)$

humic acids. Since the relative intensity of doublet increases with the increase in HA concentration, the relative iron content in the interface increases. The core of the nanocomposite as the initial substance is a mixture of non-stoichiometric magnetite and maghemite.

Humic acid adding to the solution leads to the size stabilization of nanoparticles and restriction of their growth.

Mössbauer measurements were carried out in a temperature range from 130 K to 300 K for the nanocomposites with 20 % HA and 50 % HA. Mössbauer spectra of nanocomposites with 20 % HA measured at temperatures of 130 K, 180 K, 256 K and 300 K are shown in Fig. 3. All spectra are the Zeeman sextets with broaden lines and it is typical of superparamagnetic particles. Spectra processing was carried out as described previously by model fitting of quadrupole doublet and extracting the distribution of the hyperfine magnetic field $p(H)$. The spectra show a gradual broadening of the lines with increasing temperature. The analysis of the spectra has also shown that the maximum of the hyperfine magnetic field distribution shifted to the region of larger field values with the decrease in temperature (Fig. 3).

We estimated the size of the nanocomposite particles using these temperature measurements. For this purpose, we obtained the parameter $\alpha = K_{\text{eff}}V/kT = \beta/T$ as a function of the inverse temperature 1/T (Fig. 4). The values β were calculated for both nanocomposites – 20 % of HA and 50 % of HA using linear approximation. Assuming that the particles are spherical with diameter d we have plotted the dependence β as a function of parameter d applying a model for effective anisotropy energy constant $K_{\text{eff}} = K_{\text{V}} + \frac{6K_{\text{S}}}{d}$ (where

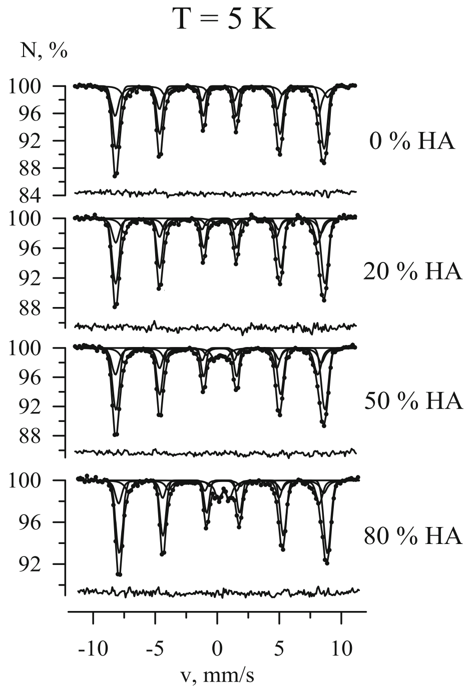


Fig. 2 Mössbauer spectra of the nanocomposites with different concentration of humic acids measured at $T = 5$ K

K_V and K_S are respectively the volume and surface anisotropy energy constants) [4]. For this relation the following constants for magnetite were used $K_V = 1.3 \cdot 10^4$ J/m^3 and $K_S = -0.7 \cdot 10^{-5}$ J/m^2 [5]. We obtained nanocomposite particle sizes using the dependence $\beta(d)$ and the values of β which were calculated for both nanocomposites: $d = 13.5 \pm 0.1$ nm (20 % HA) and $d = 12.3 \pm 0.1$ nm (50 % HA).

4 Magnetic measurements

Magnetization measurements were carried out at the temperature of 80 K, 190 K and 300 K. The hysteresis loops measured at 80 K for nanocomposites with different HA concentration obtained by chemical precipitation method are shown in Fig. 5. The form of magnetization curves of the samples is characteristic of ferromagnetic materials. The change in the hysteresis loops parameters was observed with changing the concentration of humic acid like precursors in the nanocomposites. It can be seen that adding of 20 % humic acid did not substantially change the magnetization curve as compared to the initial sample. However, at 50 % and 80 % the hysteresis loops become narrower. Hysteresis loop narrowing is also observed with decreasing measurement temperature. This behavior is due to a decrease in the thermal fluctuation energy of the magnetic moment of the nanocomposites particles.

The coercive force (Hc) and the saturation magnetization (Ms) for different nanocomposites defined from hysteresis loops were recalculated per unit volume, using the average density of nanocomposites equal to 2 g/cm^3. The analysis of the parameters of hysteresis loops showed that the coercive force decreased with increasing temperature. This

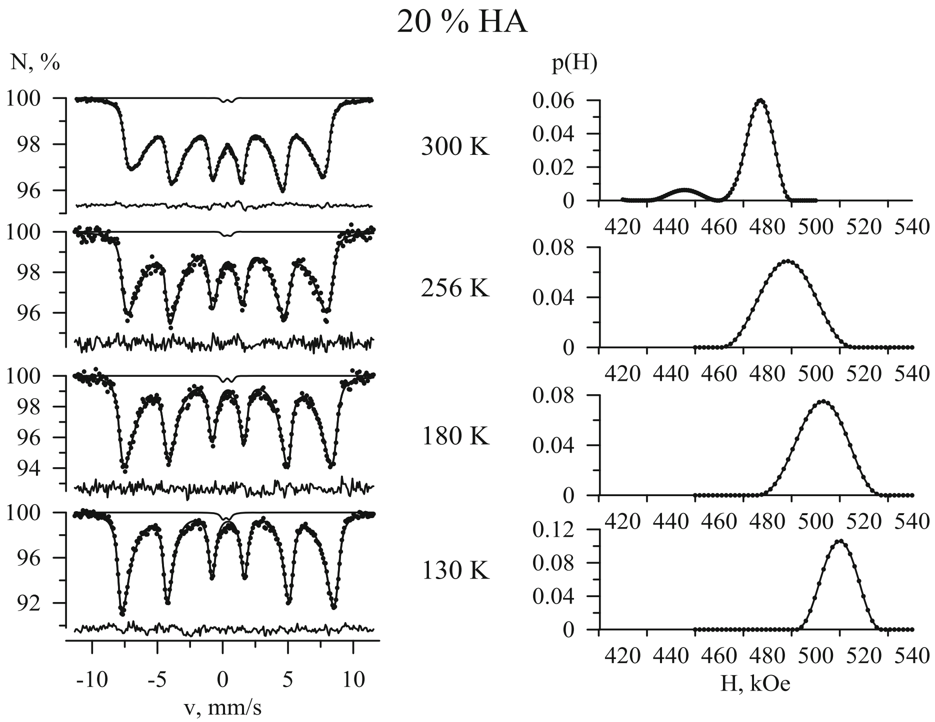
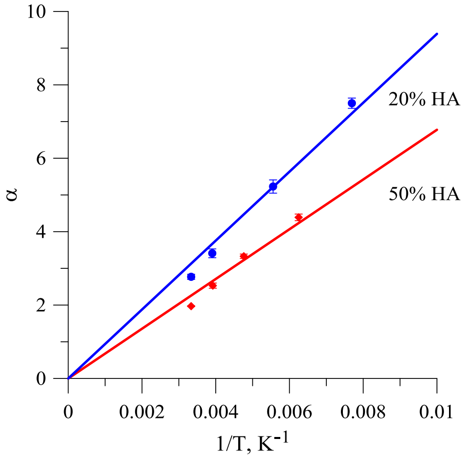


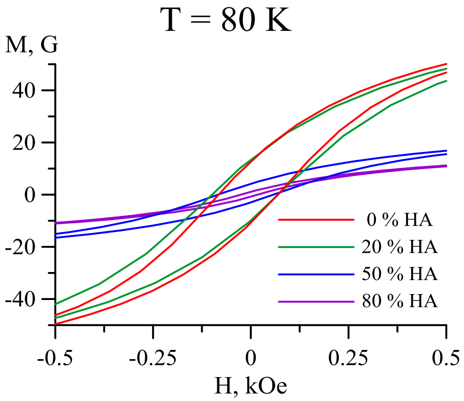
Fig. 3 Mössbauer spectra and corresponding distributions of hyperfine magnetic field $p(H)$ of the nanocomposite with concentrations of humic acids equal to 20 % measured at different temperatures

Fig. 4 The values of parameter α obtained at different temperatures as a function of $1/T$ (linear approximation)



behavior of the coercive force was also observed earlier [6] but the calculated values of coercive forces at room temperature were less than the corresponding values obtained in [7] for the maghemite nanoparticles. The humic acid concentration changing from 20 % to 50 % does not virtually change the coercive force. However at 80 % the coercive force decreases several times.

Fig. 5 Magnetic hysteresis loop for nanocomposite samples measured at $T = 80$ K



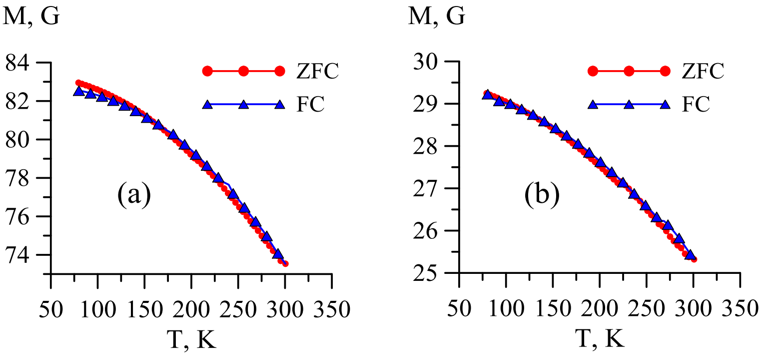


Fig. 6 ZFC and FC curves for nanocomposites with 20 % (**a**) and 50 % (**b**) of humic acids

The temperature dependences of the magnetization in an external magnetic field (10 kOe, temperature range 80 ÷ 300 K) in the ZFC/FC regime are shown in Fig. 6. The ZFC and FC curves do not separate as the blocking temperature for magnetite nanoparticles is less than 50 K [8]. However, the value of magnetization is higher for the sample with low concentration of the humic substances that can be explained by the decrease in particles size with the increase of humic substances concentration [8]. This result correlates with the data obtained by Mössbauer spectroscopy.

5 Summary

Nanocomposites containing iron oxides and humic acids have been studied by Mössbauer and magnetic measurements. The following results have been obtained.

Particles of the investigated nanocomposites exhibit superparamagnetic properties.

The core of the nanocomposite is a mixture of non-stoichiometric magnetite and maghemite.

The "iron-polymer" interface is formed on the surface of the particles as the result of the interaction of iron oxides and humic acids. The subspectrum parameters of ^{57}Fe nuclei in the interface structure correspond to Fe^{3+} atoms in the octahedral environment of oxygen atoms. The relative iron content in the interface increases with increasing the humic acids concentration.

The sizes of nanocomposite particles decrease with increasing the HA concentration: d (20 % HA) = 13.5 ± 0.1 nm, d (50 % HA) = 12.3 ± 0.1 nm.

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