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Influence of interactions to the properties of ultrasmall $CoFe_2O_4$ nanoparticles estimated by Mössbauer study

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ABSTRACT

Superparamagnetic properties of ultrasmall $CoFe_2O_4$ (1–3 nm) nanoparticles before and after gold plating were studied by Mössbauer spectrometry. The nanoparticles in the suspension in water were compared with same dried nanoparticles. Blocking temperature increases by 10–20 K after drying of the suspension. Strong dipolar and indirect exchange interactions between nanoparticles in the dried state were used to explain observed differences. The strength of interactions was estimated by the application of the multilevel model for the description of Mössbauer spectra. The strength of interactions between nanoparticles in the dried state, as it was observed, decreased with temperature. Moreover, the multilevel model allowed us to determine the superparamagnetic relaxation time and the barrier height. The results indicate that magnetic anisotropy of $CoFe_2O_4$ nanoparticles should be similar to the anisotropy of bulk $CoFe_2O_4$.

1. Introduction

The properties of materials in nanostructures may markedly change [1]. Particularly, magnetic properties also alter due to nanoscale effects [2], for example, the superparamagnetism of single domain nanoparticles [3]. Superparamagnetic nanoparticles as the main constituent are used in ferrofluids applicable in nanotechnology [4–6]. Moreover, magnetic nanoparticles can be used for a separation of cells, the hyperthermia treatment, as carriers of drugs in medicine [7–11]. $CoFe_2O_4$ nanoparticles in comparison with iron oxide nanoparticles have higher magnetic anisotropy and can be beneficial, for example, in hyperthermia applications [12,13]. Furthermore, the size effects on properties can be particularly interesting to study, especially in the case of ultrasmall $CoFe_2O_4$ (1–3 nm) nanoparticles. Enhanced magnetization [14] and the reduction in Curie temperature [15] were reported for $CoFe_2O_4$ nanoparticles. A dependence of magnetic anisotropy on the size of $CoFe_2O_4$ particles was also observed [16]. However, the studies of nanoparticles are complicated due to the influence of size distribution and interactions between the nanoparticles [17–19]. Strong interactions between superparamagnetic nanoparticles can lead to the magnetic (superferromagnetic) ordering above a blocking temperature characteristic of not interacting nanoparticles [3,19]. The superferromagnetic state of nanocrystalline antiferromagnetic goethite was explained by a partial exchange coupling between the surface atoms of neighboring nanoparticles [18,20]. It was shown that dipolar interactions can also be responsible for the superferromagnetic state in ordered 1D and 2D assemblies of superspins [3,21]. However, the weak exchange interactions may have an important role stabilizing the superferromagnetic ordering observed for the assemblies of dipolar interacting Fe nanostripes, isolated Fe, FeCo and Co nanoparticles in a nonmagnetic matrix [22–27].

The superparamagnetic nanoparticles are frequently characterized by blocking temperature which can be determined by means of different methods including Mössbauer spectrometry [28]. However, blocking temperature depends on both superparamagnetic properties of nanoparticles and characteristic measurement time of the applied method. The superparamagnetic dynamics of the magnetic moment of a nanoparticle can be described by the application of a multilevel model which allows obtaining the temperature dependent shape of Mössbauer spectra of superparamagnetic nanoparticles [29–31]. Herein, the multilevel method is used to evaluate properties of ultrasmall $CoFe_2O_4$ nanoparticles prepared by co-precipitation way using Mössbauer spectroscopy data at temperatures near superparamagnetic blocking temperature. The influence of interactions is investigated using a comparison of same nanoparticles in the frozen suspension in water with them in a dry state.

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2. Experimental

$CoFe_2O_4$ nanoparticles are synthesized by co-precipitation method using $CoCl_2$, $Fe_2(SO_4)_3$ and NaOH at 80 °C temperature and 12.0 pH [32]. The citric acid which acts as an electrostatic stabilizer [11] is added to make stable suspensions of nanoparticles in water. The size of nanoparticles (2–3 nm) is evaluated by means of AFM and TEM (Fig. 1). Previously prepared $CoFe_2O_4$ nanoparticles are covered with Au with an assistance of Vitamin C at 6.0 pH by an addition of HAuCl during two days as described in Ref. [33].

Mössbauer transmission spectra were collected using the Mössbauer spectrometer with a source of ^{57}Co(Rh) and the closed cycle helium cryostat (Advanced Research Systems, Inc.). 2 ml of suspensions either of $CoFe_2O_4$ or $CoFe_2O_4$@Au nanoparticles in water (the concentration of $CoFe_2O_4$ was 0.1% of volume) were placed in the special cell for low temperature measurements. After the measurements the suspensions were dried on a filter paper and measured again at same temperature region.

Superparamagnetic blocking temperature T_B of ultrasmall $CoFe_2O_4$ nanoparticles is determined using the dependence of average hyperfine field $\langle B\rangle$ on temperature (Fig. 2a) at $\langle B\rangle \approx 0.5B_0$. Average hyperfine field is evaluated by fitting of a hyperfine field distribution and a superparamagnetic singlet/doublet to Mössbauer spectrum using Normos Dist software. Average hyperfine field is obtained by the expression $\langle B\rangle = \frac{\sum P_i B_i}{\sum P_i + P_s}$, where P_i is the relative area of sextet having the hyperfine field B_i in the hyperfine field distribution. The hyperfine field $B_0 \approx 53.4$ T is the average hyperfine field of a bulk $CoFe_2O_4$ when $T \to 0$ [34,35]. Blocking temperature is also frequently determined at temperature when the area of paramagnetic part P_s is equal to the area of magnetically split part of Mössbauer spectra P_m (Fig. 2b). In this case blocking temperature (T'_B), as it is obtained, is larger by 11–18 K than T_B (Table 1). It is because $\langle B\rangle$ is affected by a change in both the area and hyperfine field distribution.

In addition, the multilevel model is used. It allows us to determine superparamagnetic relaxation time τ as well as other parameters. A line shape of Mössbauer spectrum in the multilevel model is given by the expression [29]:

$$I(\omega) = 2\,\mathrm{Re}(\mathrm{WM}^{-1}\mathbf{1}) \tag{1}$$

where elements of the matrix **W** are the occupation probabilities of the levels. The levels are associated with the projections S_z of the spin S to the easy magnetic axis and are used to describe dynamics of a magnetic moment of a nanoparticle. The diagonal matrix $\mathbf{\Omega}$ in the matrix $\mathrm{M}=i(\omega+\Gamma)\,\mathrm{I}+\mathbf{\Omega}+\mathbf{\Pi}$ describes the static positions of Mössbauer spectrum associated with the levels. The matrix **I** is a diagonal unit matrix and the matrix $\mathbf{\Pi}$ describes a relaxation rate which is determined by the diffusion parameter R and the energy difference between levels. The probability of a jump to the level having higher energy is $R\cdot\exp(-\Delta E/k_BT)$ where k_B is the Boltzmann constant, T is temperature and ΔE is the energy difference between the adjacent levels. When magnetic field H acting on magnetic moment of a nanoparticle m is collinear to easy magnetic axis magnetic energy of a nanoparticle:

$$E = KV\,\sin^2\theta - \mu_0 mH\,\cos\,\theta \tag{2}$$

depends only on one angle θ. KV (K is the magnetic anisotropy constant and V is a volume of a nanoparticle) is uniaxial magnetic anisotropy energy, θ is the angle between magnetic moment of the particle and the easy magnetic axis and μ_0 is the vacuum permeability. The magnetic moment of a nanoparticle $m = M_sV$ where M_s is volume magnetization. The Eq. (2) defines the energy of the levels because of $\cos\theta = S_z/S$. In the case of strong dipolar interactions between nanoparticles when nanoparticles order in chains or in assemblies of interacting nanoparticles (superferromagnetism) magnetic moments arrange mostly in parallel [18,19].

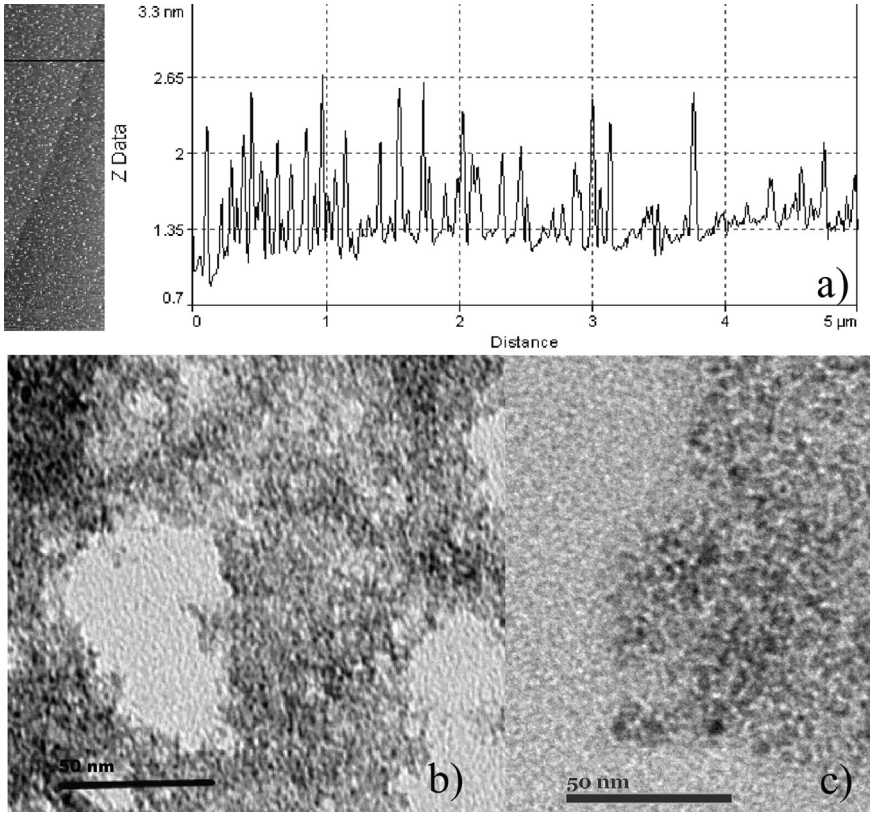

Fig.1. AFM data (a) and TEM images of $CoFe_2O_4$ (b) and $CoFe_2O_4$@Au (c) nanoparticles.