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Superparamagnetism in Cobalt Nanoparticles Coated by Protective Gold Layer

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In this work we present the study on structural and magnetic properties of fine cobalt nanoparticles coated by protective gold layer synthetized by microemulsion method. Structural measurements (powder XRD, HRTEM) confirmed spherical shape of the particles, their nanocrystalline character and presence of individual Co and Au phases. Investigation of magnetic properties of the particles revealed superparamagnetic behavior at higher temperatures and magnetic hysteresis at low temperatures. Average magnetic moment of individual particle $m_p \sim 86.3\mu_B$ was established. The critical temperature, below which the magnetic moments of the particles are blocked, was $T_B = 6$ K. Investigation of magnetic relaxation processes via magnetic susceptibility, detected one maximum attributed to single relaxation process, present in the particles. Obtained data, interpreted in terms of Neél-Arrhenius and Vogel-Fulcher theoretical models, confirmed the presence of strong magnetic interparticle interactions.

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1. Introduction

Magnetic nanoparticles are investigated nowadays not only for their spread applications [1], but also due to their potential to reveal new properties and nature of behavior of the nano-scaled structures [2]. In this paper we deal with magnetic properties of cobalt nanoparticles coated by protective gold layer. Due to the small size of the particles, the cobalt core is in the state of single magnetic domain possessing a huge magnetic moment. Gold coating preserves the core from oxidation and makes the particles biocompatible. These properties predestinate studied bimetallic nanoparticle system for possible use in biomedical applications (MRI, hyperthermia) [1].

2. Experimental

The investigated nanoparticles were synthetized employing the microemulsion method. Structural analysis was performed by High-resolution transmission electron microscopy (HRTEM) and High energy powder X-ray diffraction (HE-PXRD). Magnetic measurements were carried out using commercial SQUID apparatus (Quantum Design MPMS 5XL) in temperature range of 2–300 K in the magnetic field up to 5 T.

3. Results and discussion

The size and shape of the prepared Co@Au nanoparticles were studied by HRTEM. The representative micrograph is shown as inset of Fig. 1. From HRTEM the presence of individual particles with the size of about 10 nm could be observed. The nanoparticles were further analyzed by HE-PXRD. The X-ray diffraction pattern is shown as inset of Fig. 2. The relatively broad Bragg peaks indicate nanocrystalline nature of nanoparticles. The positions of diffraction peaks identified the presence of individual Au and Co phases.

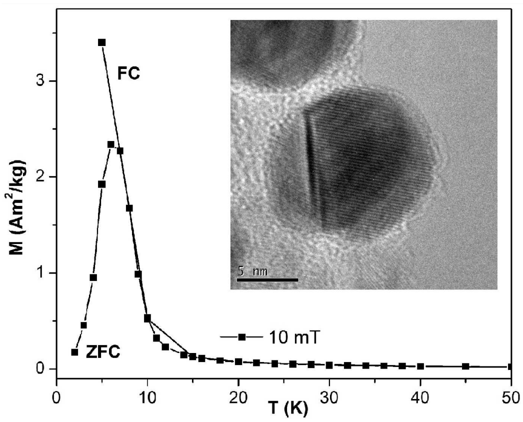

Fig. 1. Temperature dependence of magnetization measured in ZFC (zero-field cooled) and FC (field cooled) protocols in low *DC* field of 10 mT. Inset shows the HRTEM picture of Co@Au nanoparticles.

The evidence of superparamagnetic behavior of the sample was revealed from the temperature dependence of magnetization measured within the range from 2 K to 300 K in low external static magnetic field. The curves $M(T)$ of the sample recorded both in ZFC (zero field cooling) and FC (field cooling) regimes exhibited the irreversibility at low temperatures (see Fig. 1). According

*corresponding author; e-mail: pavol.hrubovcak1@student.upjs.sk to [3] the position of the maximum of ZFC curve can be attributed to the critical temperature T_B of the particles. With regard to [3] we determined the blocking temperature $T_B \sim 6$ K (Fig. 1). Above the blocking temperature magnetic moments of the particles freely fluctuate trough the energy barrier, leading to the superparamagnetic relaxation. Below blocking temperature T_B the magnetic moments of the particles are blocked in external DC magnetic field and the sample exhibits hysteresis with the coercivity $H_C = 118$ mT, see Fig. 2.

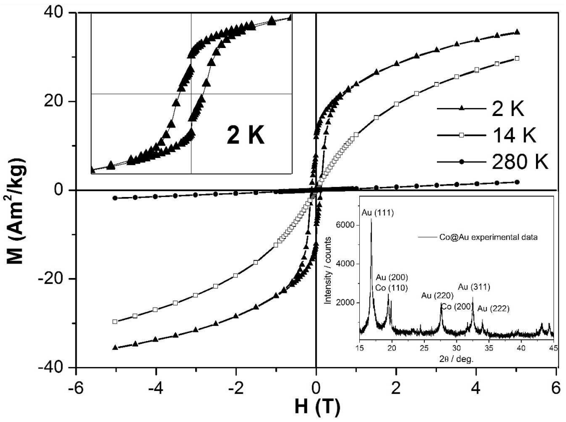

Fig. 2. Field dependence of magnetization measured at different temperatures of 2 K (triangles), 14 K (empty squares) and 280 K (circles). Inset shows the hysteresis loop of the sample measured at the temperature of 2 K.

Since the presence of superparamagnetic behavior in our sample above blocking temperature, we have used the Langevin analysis [4]. Applying Langevin fit to the experimental data measured at 280 K, we obtained the average values for the magnetic moment and the diameter of particles, $m_P \sim 86.33$ μ_B and $d \sim 5.36$ nm, respectively. The lower value of the particle size obtained from Langevin fit in comparison with the HRTEM results can be attributed to the fact, that the magnetization data used for the calculations, considered only the contribution from ferromagnetic cobalt core, not the Au shell.

In order to investigate the presence of magnetic interactions between the particles we have examined the dynamic properties using complex AC susceptibility in the temperature range of 2–300 K measured at different frequencies (0.1–1000 Hz). The experimental data displayed single maximum in the in-phase AC susceptibility $\chi'(f,T)$ (real component) curve (Fig. 3). With increasing frequency the maxima of both $\chi'(f,\ T)$and $\chi''(f,T)$ curves shift towards higher temperatures and the magnitude of the peaks increases and decreases, respectively.

Quantitative analysis of experimental $\chi'(f,T)$ data was performed employing Neél-Arrhenius and Vogel-Fulcher models [4]. From such analyses the value of pre-relaxation constant $\tau_0 = 1.5 \times 10^{-14}$ s estimated from Vogel-Fulcher law, predicts the presence of the strong dipolar interactions between nanoparticles. Also analyses of experimental data from AC magnetic susceptibility using the frequency dependent criterion $p = 0.02$ [4] confirms that inter-particle interactions in prepared nanoparticle system are non-negligible.

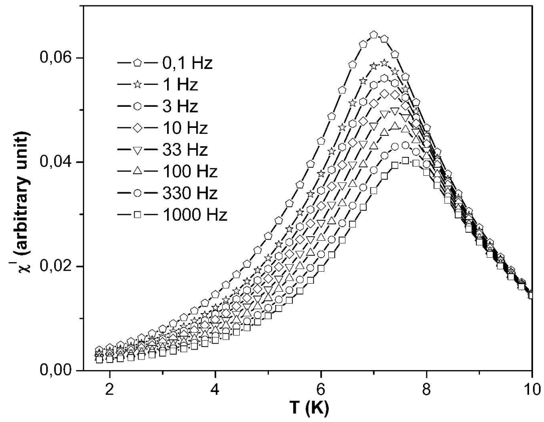

Fig. 3. Temperature dependence of in-phase $\chi'(T)$ AC susceptibility (real part) measured at different frequencies of AC field in the temperature region from 2 K to 10 K.

4. Conclusions

We have synthesized the fine superparamagnetic Co nanoparticles coated by Au layer with spherical shape and the average diameter about 10 nm. The average magnetic moment of each particle was estimated to $m_P \sim 86.33$ μ_B. From the maximum of ZFC curve the value of blocking temperature was determined to $T_B = 6$ K. The analysis of dynamic magnetic properties of the sample showed the presence of strong dipolar magnetic inter-particle interactions.

Acknowledgments

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