Magnetic properties of Fe₂O₃ nanoparticles embedded in hollows of periodic nanoporous silica

A. Zeleňáková,^{1,a)} J. Kováč,² and V. Zeleňák³

¹Department of Solid State Physics, P.J. Šafárik University, 04154 Košice, Slovakia

²Institute of Experimental Physics, Slovak Academy of Sciences, 040 01 Košice, Slovakia

³Department of Inorganic Chemistry, P.J. Šafárik University, 04154 Košice, Slovakia

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The magnetic properties of the nanocomposite consisting of hematite (α -Fe₂O₃) nanoparticles embedded in the hollows of the periodic nanoporous silica matrix were investigated. The magnetic measurements showed on the superparamagnetic behavior of the nanoparticles. This behavior was evidenced by the irreversibility of magnetization curves measured in zero-field-cooled and field cooled regimes, by the presence of a maximum in zero-field-cooled magnetization curve related to blocking temperature $T_B \sim 37$ K and also by revealing of the coercivity H_C below T_B . The value of the magnetic moment $m_p \sim 300 \mu_B$ of each iron-oxide particle was estimated. The interparticle interactions were investigated from dynamic properties using ac susceptibility. The susceptibility study shows, that the in-phase ac susceptibility χ' is frequency dependent and the peak position increases with the increase in the frequency. The quantitative analysis of χ' using theoretical models shows on the existence of weak dipolar interactions between particles. It was shown from correlation of experimental data with Arrhenius and Vogel–Fulcher laws that the incorporation of the nanoparticles into porous SiO₂ matrix provides the effective method for the reducing of dipolar interactions between magnetic nanoparticles with the size below 10 nm. © 2010 American Institute of Physics. [doi:10.1063/1.3466748]

I. INTRODUCTION

Nanoparticles attract nowadays considerable research attention because they are expected to be useful as novel materials for biological applications (e.g., magnetic carriers of drugs, MRI contrast agents), or in various devices such as memories, batteries, and displays showing enhanced properties.^{1,2} Recent progress in the electronics and information technologies resulted in the necessity to develop high-density storage devices and new techniques for ultrahigh density recording.³ One of the effective ways to densely pack the magnetic nanoparticles, with the possibility of controlling their size and shape, is the growth of the nanoparticles in the periodic structures. In this nanotechnology approach, called “nanocasting,” the periodic porous silica materials are employed as hard templates and act as nanoscopic molds. Various metal or metal oxides can be grown in the silica matrix creating nanocomposites with interesting magnetic properties and rigid structure.^{4,5}

The stability of electronic and high-density data storage devices made of magnetic nanocomposite is limited by their superparamagnetic transition.³ Therefore, there is a strong interest to understand the magnetization processes in the superparamagnetic region. The current efforts are aimed at increasing of the thermal energy barrier against the magnetic reversal in magnetic nanocomposite. However, for the applicability of densely packed magnetic nanoparticles it is also important to know, how the interparticle interactions affect the physical properties of the system.^{6–9} The influence of the interparticle interactions on magnetic properties was studied

by several works.^{6–11,13–17} The interparticle interactions can increase the media noise and therefore the high-density recording requires the grains to be isolated to minimize the dipolar interactions. Strong dipolar interactions were observed in hematite nanoparticles prepared by different chemical ways.¹⁸ On the contrary, the reduction in the interparticle interactions was observed after the chemical coating of nanoparticles by a nonmagnetic shell¹⁸ or by the loading to the polymer matrix.^{10,11,16,17}

In this context, we have studied magnetic properties of Fe₂O₃@SiO₂ composite prepared by nanocasting of iron oxide (α -Fe₂O₃, hematite) in periodic nanoporous SBA-15 silica matrix. The interparticle interactions were investigated using dynamic properties of the system. The data of ac magnetic susceptibility have been analyzed through Arrhenius and Vogel–Fulcher laws and through frequency-sensitive parameter p with the aim to quantify the degree of interaction between magnetic moments of the particles.

II. EXPERIMENTAL PROCEDURE

A. Preparation of nanocomposite

The magnetic nanocomposite, build up from hematite nanoparticles loaded in the channels of hexagonally ordered silica matrix, were prepared via the nanocasting approach. The periodic silica matrix of SBA-15 type was synthesized using tetraethoxysilane as a silica source and poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) block copolymer Pluronic P123 as a templating agent. Prior the synthesis of iron oxide particles in the pores of SBA-15 the external surface of SBA-15 was modified to be more hydrophobic. Cyclohexyl-methyldimethoxysilane was used for the

^{a)}Electronic mail: adriana.zelenakova@upjs.sk.

surface modification. The nanocomposite $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ was synthesized by wet-impregnation of the prepared porous matrix using precursor containing Fe^{2+} ions followed by their reduction with NaBH_4 . After reduction the sample was calcined in air at 500 °C.

B. Characterization of nanocomposite

The microstructure of the prepared nanocomposite was investigated using high-resolution transmission electron microscopy (HRTEM) micrographs taken with a JEOL JEM 3010 microscope. Copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation. Long range order and symmetry of nanocomposite, its phase analysis we investigated by a synchrotron related techniques small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS). The SAXS experiments were carried out at B1 Hasylab beamline (DESY Hamburg) with the beam energy 12 keV ($\lambda=1.03$ Å). The WAXS was measured at BW5 Hasylab beamline (DESY Hamburg), at the wavelength $\lambda=0.123\,980$ Å. Magnetic measurements were performed on a commercial superconducting quantum interference device-based magnetometer (Quantum Design MPMS 5XL) over a wide range of temperatures (2–300 K) and applied dc fields (up to 50 kOe). Complete magnetization curves (M versus H), including the virgin magnetization curves, were measured by a standard procedure from the field -50 to $+50$ kOe. The temperature dependence of the dc magnetization was measured in zero-field-cooled (ZFC) and field cooled (FC) regimes in a low static field. Starting from ZFC regime, the sample was cooled to 2 K without applying external field and then the magnetization was recorded in temperature range 2–300 K under the dc field. Subsequently, the sample was cooled to 2 K in external field with simultaneous recording of magnetization, what is represented by FC curve. The ac magnetic susceptibility measurements (in-phase χ' and out-of-phase χ'' ac susceptibility) were carried out using at frequencies 1–1000 Hz in a temperature region 2–300 K.

III. RESULTS AND DISCUSSION

A. Structural properties

The prepared composite sample was structurally characterized by HRTEM, SAXS, WAXS, and nitrogen adsorption measurements. The detailed structural study was described elsewhere.¹² The results of the HRTEM (see Fig. 1) confirm the regular honey-comb structure of the composite sample. The pore size of the silica matrix, as estimated from HRTEM micrographs, was approximately 7 nm. The center-to-center distance of the channels was about 10 nm (7 nm size of the cylinder plus 3 nm the wall thickness). For detailed assessment of the pore size the nitrogen adsorption/desorption experiments were used.¹² The pore size, as calculated from adsorption branch of the isotherms according to Barrett–Joyner–Halenda (BJH) model ($D_{\text{BJH}}=7.1$ nm), was in good agreement with the HRTEM observations.

The analysis of the iron oxide phase composition by wide angle x-ray powder diffraction (WAXS) and by X-ray Absorption Near Edge Spectra (XANES) at Fe K -edge show,

FIG. 1. HRTEM micrographs of the $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ nanocomposite sample. (a) View along the hexagonal axis and (b) view perpendicular to the hexagonal axis.

that iron oxide particles are formed by pure hematite ($\alpha\text{-Fe}_2\text{O}_3$) phase.¹² The x-ray diffraction data were used for estimation of the particle size by Scherrer formula. The calculated value of the crystallite sizes was $d=5$ nm.

B. Magnetic properties

The size of the prepared nanoparticles fall within the region, where the particles behave as single magnetic domains and therefore we expected to observe their superparamagnetic nature by magnetic measurements. Magnetic measurements in dc magnetic field (temperature and field dependence of the magnetization), recorded in temperature range from 2 to 300 K in the external field up to 50 kOe, show on the superparamagnetic behavior of $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ nanocomposite (see Fig. 2). The temperature dependence of the dc magnetization in both obvious protocols, i.e., ZFC magnetization and FC magnetization measured in a low static field (see inset of Fig. 2) shows on the high irreversibility of ZFC/FC curves and the existence of the maximum in ZFC magnetization curve. The blocking temperature T_B , representing the process of blocking/freezing of magnetic spins in the nanocomposite, was observed at the temperature about 37 K (maximum in ZFC curve). Above T_B the magnetic moments of the particles freely fluctuate in the external magnetic field leading to superparamagnetism. On the contrary, below T_B , the magnetic moment of each particle is blocked in the external field direction and the hysteresis H_C

FIG. 2. The magnetic properties in dc external magnetic field. Magnetization curves (M vs H) at significant temperatures of 2 and 300 K. Inset: temperature dependence of magnetization measured in ZFC and FC regimes in dc external field of 500 Oe.

with coercivity about ~ 1890 Oe was observed (see Fig. 2). The value of the effective magnetic moment $m_p \sim 300 \mu_B$ of each particle was estimated from the room temperature magnetization curve using distribution of the Langevin functions. Since the magnetic moment of the particle is related with the spherical particles diameter d through relation $\mu = M_s(\pi d^3/6)$, it allowed us to calculate the particle size from magnetic measurements $d = 7$ nm. The calculated value is comparable with the value determined from Scherrer formula ($d = 5$ nm).¹²

For potential applications of magnetic nanocomposite in magnetic recording media, it is necessary to know how different parameters affect the relaxation time in order to avoid spontaneous data erasure in the lifetime of the device (caused by thermal fluctuation). Because of the ongoing effort to increase the information/volume ratio, it is of special importance to know how the dipolar interactions of the nanoparticles affect the relaxation time.⁶ Therefore we realized the ac susceptibility measurements at different frequencies (1–1000 Hz) which helped us to get a deeper understanding of dynamic behavior in $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ nanocomposite.

When an ac field with frequency f is applied to a magnetic system with a distribution of relaxation times τ , the magnetic susceptibility is given as $\chi(f, T) = \chi'(f, T) + i\chi''(f, T)$, where χ' represents in-phase (real part) susceptibility and χ'' out-of-phase (imaginary part) susceptibility. It is evident from Fig. 3 that the in-phase ac susceptibility (χ') is frequency dependent and the peak position increases with increasing frequency. Data of ac susceptibility measured at frequencies in the range 1–1000 Hz exhibit the behavior typical for blocking/freezing processes i.e., the presence of a maximum in real component of dynamic susceptibility $\chi'(T)$ (in-phase ac susceptibility) at the temperature $T_{\max}$, which shifts toward higher temperatures with increasing frequency [Fig. 3(a)] and, the absorption component of ac susceptibility $\chi''(T)$ (out-of-phase ac susceptibility), which exhibits a sudden onset near $T_{\max}$ [see Fig. 3(b)]. The observed behavior in the ac susceptibility measurements may be caused by different relaxation processes as follows: (i) by the blocking of the noninteracting (weakly interacting) particles, (ii) by the

FIG. 3. The magnetic properties in ac magnetic field. (a) Temperature dependence of real component of ac susceptibility (in-phase ac susceptibility) at different frequencies in range (1–1000 Hz). The arrow indicates increasing frequencies. (b) Comparison of the in-phase χ' and out-of-phase χ'' dynamic susceptibility at 10 Hz frequency. The plots are off-set to facilitate comparison between the two components of the ac magnetic susceptibility.

blocking/freezing process of interacting particles with disordered surfaces, and (iii) by the spin-glass like behavior caused by collective freezing of strongly interacting spins.

To identify the dynamic behavior of blocking/freezing processes, we have used the real part of ac susceptibility $\chi'(T)$ through relation:^{13,14}

$$p = \frac{\Delta T_{\max}}{T_{\max} \Delta \log f}, \quad (1)$$

where $T_{\max}$ is the average value of the frequency dependent blocking/freezing temperature determined by the maximum of ac susceptibility, while $\Delta T_{\max}$ denotes the difference between $T_{\max}$ measured in the $\Delta \log f$ frequency interval. The frequency-sensitive parameter p is a simple approach to quantify the degree of interaction between magnetic moments and provides a model-independent classification of the blocking/freezing process.^{13–15} The values of parameter p are usually in the range of 0.100–0.130 for noninteracting superparamagnetic particles, whereas for magnetically interacting systems, like spin glasses, the values of parameter p are observed in the range of 0.005–0.050.¹⁴ We have calculated the value of parameter p from the experimental data using Eq. (1). The calculated value of $p = 0.093$ shows on the noninteracting or only weakly interacting superparamagnetic particles.

According to the superparamagnetic model,¹⁵ the temperature $T_{\max}$, at the maximum of in-phase ac susceptibility

$\chi'(T)$ corresponds to the blocking temperature T_B . The Néel theory of the superparamagnetism predicts that the magnetic moments of noninteracting particles with uniaxial anisotropy thermally fluctuate between two directions of easy axes. The anisotropy energy creates two potential wells separated by the energy barrier. The characteristic time for the over-barrier rotation τ (relaxation time) can approximately be written in the Arrhenius form:

$$\tau = \tau_0 \exp \frac{E_A}{k_B T_{max}}, \quad (2)$$

where E_A is the energy barrier to magnetization reversal ($E_A \sim K_{eff}V$), T_{max} is the blocking temperature, and τ_0 is the attempt frequency. The values of τ_0 are usually in the range 10^{-9} – 10^{-12} s for noninteracting superparamagnetic particles.¹³ Applying the Eq. (2) to our experimental data we calculated the value of $\tau_0 = 1.45 \times 10^{-13}$ s. This value is a little below the limit characteristic for noninteracting superparamagnetic particles. Thus the results of the characterization of interparticle interactions by parameter τ_0 agree with the results obtained from the frequency-sensitive parameter p , determined from the real part of ac susceptibility $\chi'(T)$, and show that nanocomposite system is composed from weakly interacting superparamagnetic particles.

Based on these results we further concentrated on the analysis of the existing weak dipolar interactions in the prepared nanocomposite $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ through Vogel–Fulcher equation:¹³

$$\tau = \tau_0 \exp \frac{E_A}{k_B (T_{max} - T_0)}, \quad (3)$$

which describes a system of magnetically interacting particles. The parameter T_0 is an effective temperature that arises from the interparticle interactions and represents the temperature for which the relaxation time diverges. T_{max} is the characteristic temperature indicating the onset of the blocking process, provided that $T_{max} > T_0$. The best fit values calculated by Eq. (3) are $\tau_0 = 6.24 \times 10^{-10}$ s, $E_A/k_B = 1125$, and $T_0 \sim 14 \pm 2$ K. The magnetic anisotropy parameter E_A/k_B , obtained from the dynamic susceptibility analysis, was used to the estimation of an effective anisotropy constant K_{eff} . The calculated value for hematite nanoparticles was $K_{eff} = 2.4 \times 10^6$ erg/cm³. This value is larger than the value for bulk hematite ($K_{eff} = 8 \times 10^4$ erg/cm³),¹⁶ and can be related to the spin canting in the surface layer of nanosized antiferromagnetic hematite particles¹² and to the encapsulation of particles into the porous matrix. Similarly to above results, the Vogel–Fulcher analysis indicates that only weakly interacting superparamagnetic particles are present in $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ nanocomposite. The best fits of experimental data to the Arrhenius law [Eq. (2)] and Vogel–Fulcher law [Eq. (3)] are shown in Fig. 4. The good agreement between experimental and simulated curves confirms only weak interaction between particles.

The existence of the noninteracting or weakly interacting nanoparticles system, which follows from our study of dynamic properties of the $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ nanocomposite, is in a good agreement with the results obtained from ZFC/FC mea-

FIG. 4. The dependence of T_{max} (estimated from ac susceptibility) on ac frequency ($\tau = 1/f$). Black solid line represents the fit using Arrhenius law [Eq. (2)] and gray solid line represents fit calculated using Vogel–Fulcher equation [Eq. (3)].

surements (see inset of Fig. 2). The FC magnetization curve in our experimental data displays a monotonic increase below T_B , while for interacting particles almost constant value of FC magnetization below T_B should be expected.

The recent ac susceptibility studies concerning the interparticle interactions between iron or cobalt based magnetic nanoparticles with the size below 10 nm showed that isolated nanoparticles exhibit the strong dipolar interactions^{16,19,20} due to the strong surface effects (caused by surface shell with different spin orientation to the bulk), which were noticeable from Vogel–Fulcher’s law analysis. As it was shown in our work, the incorporation of the nanoparticles into the rigid diamagnetic SiO_2 matrix with the wall thickness about 3 nm provides the effective method for the reducing of dipolar interactions between magnetic nanoparticles.

IV. CONCLUSIONS

The magnetic properties of $\text{Fe}_2\text{O}_3 @ \text{SiO}_2$ nanocomposite were investigated. Magnetic measurements confirm a behavior typical for a superparamagnetic system, such as the irreversibility of the ZFC and FC curves, presence of a maximum in ZFC curve related with blocking temperature $T_B \sim 37$ K and revealing of coercivity H_C below T_B . The interparticle interactions were investigated using dynamic properties of the system (ac susceptibility). The analysis of ac magnetization study shows, that the dipolar interactions between the hematite particles with the size about 5 nm are weak, characterized by the values of $\tau_0 = 6.24 \times 10^{-10}$ s. Particles densely packed in the ordered nanocomposite exhibit the value of anisotropy $K_{eff} = 2.4 \times 10^6$ erg/cm³. From the study it follows, that the loading of the magnetic nanoparticles into periodic nanoporous SiO_2 matrix shows several advantages as follows: (i) prevents the agglomeration of the particles, which influence the magnetic relaxation processes, (ii) the particles nanocasted in nanoporous matrix exhibit the narrow particle size distribution, (iii) loading of the nanoparticles into periodic porous silica matrix can suppress their interparticle interactions. Since the interparticle interactions can negatively influence the media noise, the loading of the

magnetic nanoparticles into rigid silica matrix, as presented in this work, may be one of the effective ways to reduce such interactions.

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