

Effect of 1D Ordering on Magnetic Properties of Iron Nanoparticles coated by Silica Shell

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Peculiar magnetic properties of 1D arranged composite consisting of Fe nanoparticles coated by insulating SiO₂ layer were studied. Silica layer promotes the self-organization of 4 nm iron nanoparticles to the chain-like structures. Magnetization study shows that prepared nanoparticles exhibit very strong inter-particle magnetic interactions, which lead to long-range ordering of nanoparticles magnetic moments. Magnetic properties show superferromagnetic behaviour. The low value of room temperature coercivity, the existence of electrical insulating silica layer and small size of iron nanoparticles favour studied material for potential usage in microelectronic devices designed for high voltage signals modulated by high frequencies.

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1. Introduction

Intensive study of magnetic nanoparticles (MNPs) in last decades led to introduction of novel magnetic states of nanoparticle systems [1–2]. Although the superparamagnetic and superspin glass behaviour [1–3] have already been documented properly, the evidence of superferromagnetism is the state of the art in the field of nanoscience. The phenomenon of superferromagnetism occurs in dense systems consisting of mono-domain magnetic nanoparticles in which the mutual inter-particle interactions are strong enough to suppress the superparamagnetic relaxation. These interactions may lead to long range magnetic ordering of the particles' superspins [2–7]. Several theories trying to explain and describe the superferromagnetism [2, 4] have been proposed, but its origin is not clear by now. According to [5], three main interactions are considered to contribute to the existence of superferromagnetic state: dipolar magnetic interactions, short range exchange interaction between the surface spins of two particles in close contact and tunnelling exchange interaction. Osaci [6] introduced the theoretical model considering the dipolar magnetic interaction with the aim to determine the transition from superparamagnetism to superferromagnetism in nanoparticle systems. This theoretical study shows the existence of critical particles' concentration at which the collective state is formed and superparamagnetic particles switch to superferromagnetic.

The different effect of silica coating on magnetic properties of MNPs was reported in [7–10]. Superparamagnetic state characterized by weak inter-particle interaction was observed in magnetic nanoparticles coated by

silica layer [7–9]. On the contrary, Salgueirino-Maceira et al. [10] confirmed the existence of the strong dipole-dipole magnetic interactions which are the driving forces of the self-organization of silica-coated cobalt nanoparticles into chains. They concluded that ferromagnetic-like behaviour was present in this one dimensional structure.

In this context, we have studied the properties of iron nanoparticles coated by silica layer, which were prepared using surface capping agents. Such designed silica layer prevents the oxidation of the iron cores and promotes the self-organization of nanoparticles into the 1D chain structures. The particular superferromagnetic state was observed in studied material.

2. Experimental part

In the first step the pure Fe nanoparticles were synthesized and their size was controlled using surface-capping agents (lauric acid (LA) and citric acid (CA)). Iron (III) nitrate, CA and LA in a molar ratio ($\text{Fe}^{3+}/\text{CA}/\text{OA}$) = 1/1/0.5 were dissolved in a 200 cm³ water/ethanol (2:1, *v/v*) mixture. Further, 20 cm³ of 0.15 M solution of NaBH₄ was dropped into the reaction mixture. Subsequently the Fe nanoparticles were coated with silica layers to prevent oxidation. Coating process was provided using APS (3-(aminopropyl) trimethoxysilane) and TEOS (tetraethyl orthosilicate). The suspension was stirred for 30 min; nanoparticles were separated by centrifugation at 4000 rpm, washed with ethanol and vacuum dried.

The HRTEM micrographs were taken with a JEOL 2100F microscope. Copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation. The bright-field TEM image was obtained at 200 kV. Energy dispersive X-ray spectroscopy (EDS) equipped within the TEM was used to determine the chemical composition of the synthesized nanoparticles. The characteristic structure of prepared sample was

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confirmed also by wide-angle X-ray scattering (WAXS) using monochromatic synchrotron radiation with beam energy of 100 keV ($\lambda = 0.12398 \text{ \AA}$). The magnetic measurements were performed on a commercial SQUID-based apparatus (Quantum Design MPMS 5XL) over a wide range of temperatures (2–300 K) and applied dc fields (up to 5 T). Zero-field cooling (ZFC) and field-cooling (FC) measurements M (T) were carried out in dc mode.

3. Results and discussion

Figure 1 shows the bright field transmission electron microscopy (TEM) images of Fe nanoparticles coated by SiO_2 shell. The average size of iron nanoparticles around 4 nm was estimated from the particle size distribution obtained from multiple TEM images. As it is seen from TEM images Fig. 1a and 1b, the Fe particles are arranged into the 1D chain. No distinct diffraction pattern is present in TEM selected area electron diffraction (SAED) pattern, Fig. 1c, what indicates the amorphous structure of prepared nanoparticles. The chemical composition of synthesized nanoparticles was revealed by the EDS spectra employing TEM, Fig. 1d. The copper and chromium signals originate from the TEM grid used in the EDS analysis.

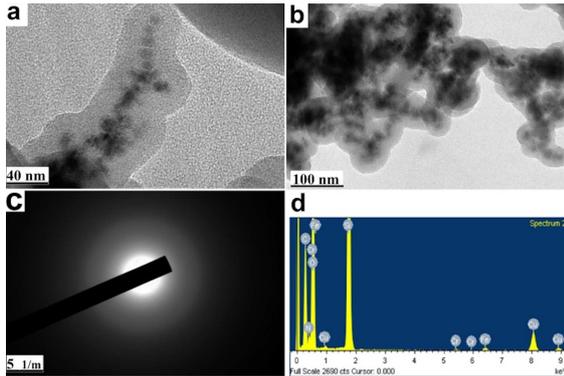


Fig. 1. HRTEM micrographs of silica coated iron nanoparticles. (a), (b) bright field TEM pictures, (c) SAED pattern, and (d) EDS spectrum.

TABLE I

Magnetic characteristics at different temperature [K].

	2	10	50	150	300	390
H_c [mT]	88	68	59	36	16	11
M_s [Am^2/kg]	18.1	16.3	13.6	12.6	11.4	9.6

Since the size of studied Fe nanoparticles is below the critical diameter, where the mono-domain character was observed and reported [1], the superparamagnetic behaviour of the system should be expected. However, the magnetic measurements carried out in dc magnetic field in temperature range from 2 K to 300 K do not suggest on typical superparamagnetic state. The field dependence of

magnetization obtained at various temperatures is shown in Fig. 2. The values of saturation magnetization M_s and the coercivity H_c at different temperatures are summarized in the Table I.

The highest value of coercivity of 88 mT was registered at 2 K. The decrease of coercivity and narrowing of hysteresis loops with increasing temperature is evident from Fig. 2. However, even at 300 K the decrease of coercivity to zero value was not observed. This result is in contradiction with expectation of superparamagnetic state typical of iron based nanoparticles with similar size [11]. These unusual properties could be explained as a consequence of very strong magnetic interactions leading to superferromagnetism in studied system.

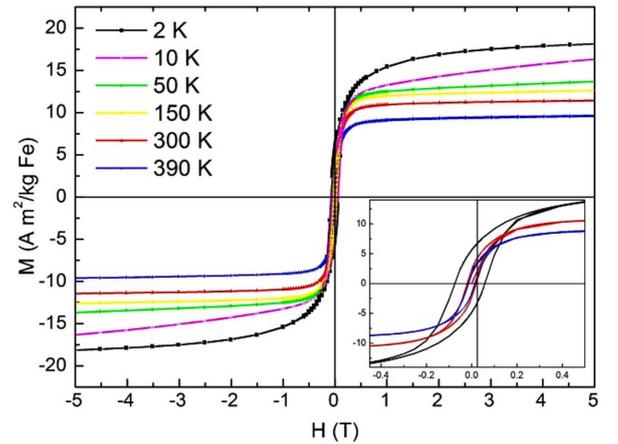


Fig. 2. Magnetization vs. magnetic field dependence obtained at various temperatures in Fe nanoparticles coated by silica shell. The values of magnetization were normalised on the Fe mass.

The temperature dependence of magnetization measured in ZFC and FC regimes is present in the Fig. 3. It is evident that the ZFC/FC curves in dc fields of 10 mT and 100 mT separate below characteristic temperature of irreversibility T_{irr} . Moreover, the ZFC curve recorded in dc field of 100 mT shows slight and almost constant increases in magnetization with rising temperature up to reaching the FC magnetization value. According to [2, 4, 5], these characteristics of thermomagnetic ZFC/FC curves are associated with a ferromagnetic behaviour.

To confirm ferromagnetic properties of the system, the $M(T)$ data measured at 500mT were fitted with the Bloch law $M(T) \sim T^{3/2}$. Results of fitting procedure clearly showed long-range ferromagnetic ordering in temperature range over 25 K.

According to studies in Ref. [12], high concentration of particles causes the close contact of their shells what enables the exchange-coupling interaction between the surface atoms from neighbouring particles.

Simultaneously, magnetic dipole interactions between nanoparticles' superspins become strong due to short particle to particle distance. Considering our experimental data that are in accordance with results presented in [12]

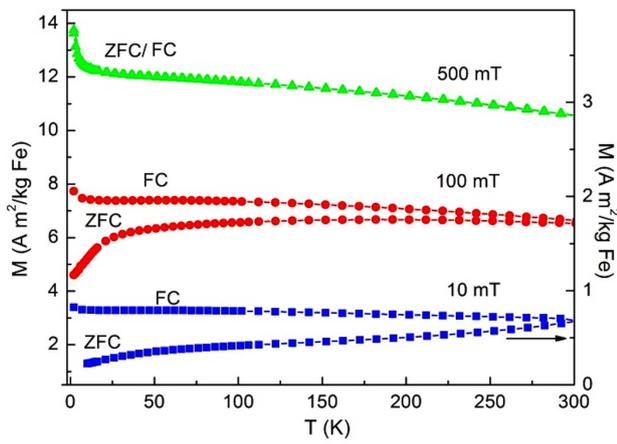


Fig. 3. The dependence of magnetization on temperature measured in ZFC and FC regimes at various external magnetic fields.

we assume that the arrangement of Fe nanoparticles in dense 1D chains promotes strong magnetic dipolar interactions, see Fig. 4. These conditions lead to long-range ordering of magnetic moments in nanoparticle ensembles and the magnetic properties of the system exhibit superferromagnetism.

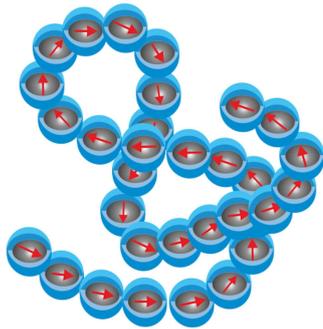


Fig. 4. Suggested schematic view on 1D chain-like structures formation in silica coated iron nanoparticles.

4. Conclusions

We have prepared and studied fine iron nanoparticles coated by silica layer. 1D chain-like structure was formed using lauric acid and citric acid as a surface capping agents together with silica coating layer. Such arrangement of mono-domain magnetic Fe nanoparticles causes the strong dipolar magnetic interactions what was confirmed by the character of ZFC/FC curves and by the existence of room-temperature coercivity. Our magnetization characteristics suggests on the presence of the peculiar superferromagnetic state in studied system.

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