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MAGNETIC PARTICLES AND NANOCRYSTALLINE MATERIALS

From Superparamagnetic to Magnetically Ordered State in Co–Sm–O Nanocrystalline Films[1]

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Abstract—Transition of the system of Co nanoparticles from a superparamagnetic state into the region of cooperative magnetic ordering caused by effects of magnetic interaction between particles has been analyzed. The possibility of the preparation of materials with soft magnetic properties and higher electrical resistivity was shown.

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1. INTRODUCTION

Magnetic nanostructures are the subject of growing interest due to potential applications for creating soft and hard magnetic materials and high-density memory devices [1, 2]. The magnetic behavior of nanostructured systems is governed by both the intrinsic properties of magnetic nanograins and the interactions between grains. In the mid-1990s, the soft magnetic properties of nanocrystalline materials were described in a number of reviews [1, 3], in which the authors reported on studies of the effect of annealing on the magnetic properties of amorphous tapes. The annealed samples consisted of magnetic grains separated by an amorphous phase whose volume fraction in the composite was ~20%. An interesting dependence of the coercive force on the diameter of the magnetic particles was discovered, which was described on the basis of the model of random anisotropy [1]. These materials can be applied at frequencies as high as several hundreds of kilohertz. To use these materials at still higher frequencies, their resistivity (ρ) must be increased.

2. FORMULATION OF THE PROBLEM

One of the methods for solving this problem is the use of nanogranular condensates in which magnetic nanoparticles are embedded into a dielectric matrix. However, the fraction of a dielectric layer should be low enough to retain good soft magnetic properties (high saturation magnetization M_s). Therefore, the potential of this approach is limited by the probability of conduction-electron tunneling through a grain boundary [4]. To further increase ρ, one can use the dependence of the charge carrier density on the particle size. The authors of [5] showed that, when the particle size was smaller than the electron mean free path, some carriers became localized. The localization was found to affect the electrical conductivity more strongly than an increase in scattering by boundaries, defects, and impurities. This effect was detected for 3*d*-metal nanoparticles with a size $D < 7$ nm.

However, in the magnetic systems with ferromagnetic particles of such a size a transition into a superparamagnetic state is observed when the thermal fluctuations exceed some threshold determined by the magnetic anisotropy. In other words, above a certain temperature (blocking temperature T_b), the ensemble of single-domain particles behaves as a gas of paramagnetic molecules with large magnetic moments [6].

In the last years, when studying the magnetic properties of nanogranular systems, a magnetic hysteresis has been revealed at temperatures above the blocking temperature. Its appearance is connected with effects of the magnetic interactions between nanoparticles. A diagram of the magnetic state of an ensemble of nanoparticles depending on the particle size and temperature has been proposed in [7] (Fig. 1).

At $T < T_b$, the system is in the ferromagnetic state. At $T > T_b$, the particles become superparamagnetic and the magnetic order remains unchanged (ISP region). The temperature of transition from the FM region to the ISP region is $T_b = KV/25k_B$ (K is the uniaxial anisotropy constant; V is the volume of a particle, and k_B is the

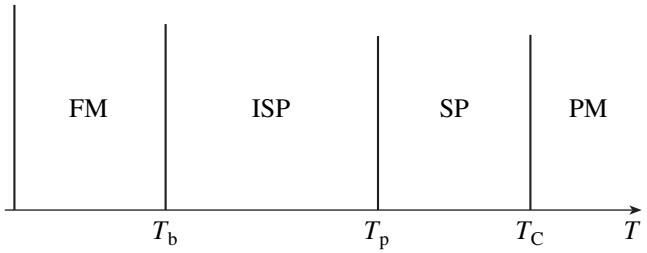

Fig. 1. Diagram of the temperature dependence of the magnetic state for an ensemble of nanoparticles (D = const).

[1] The text was submitted by the authors in English.

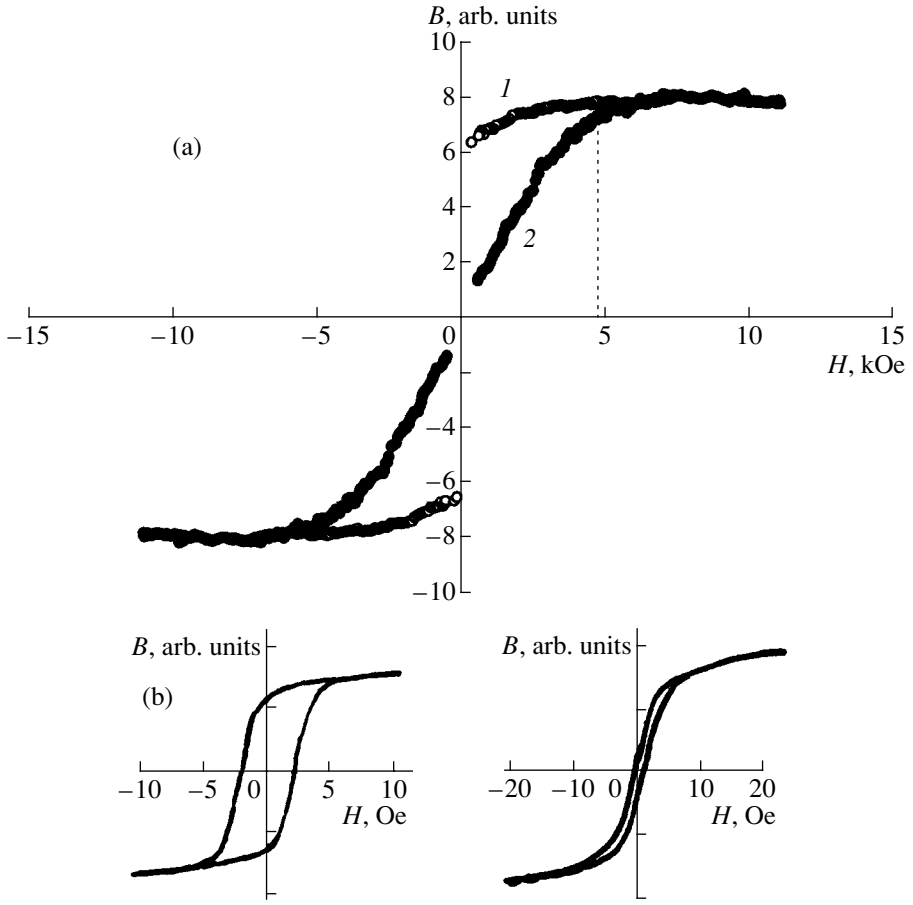

Fig. 2. (a) Curves of the magnetization reversal for films annealed in a vacuum at $T = 530$ K at a magnetic field applied (*1*) in the film plane and (*2*) in the direction normal to the film; (b) characteristic hysteresis loops in the directions of the easy and hard axes.

Boltzmann constant). At $T > T_b$, a magnetic ordering arises in the system due to the effects of magnetic interparticle interaction. In this case, the temperature of the transition to the region of a superparamagnetic (SP) state is $T_p = K_m M^2(T)/3k_B$ (K_m is the constant of magnetic coupling, M is the magnetization of particles).

Region II in the diagram ($T_b < T < T_p$) is called the region of interacting superparamagnetic particles (ISP) [8]. At $T > T_p$, the system transforms into the superparamagnetic state, and, at $T > T_C$, into the paramagnetic state (T_C is the Curie temperature).

These data show that in the ensemble of interacting superparamagnetic particles, a magnetic ordering can be created with a high ρ, since $D < 7.0$ nm.

3. EXPERIMENTAL RESULTS AND DISCUSSION

In this work, we present the results of studies of nanogranular films prepared by pulsed plasma sputtering of a $SmCo_5$ target in an initial vacuum of 10^{-6} Torr [9]. The thickness of the samples was ~100 nm. For the films obtained, the influence of the annealing on the structure, magnetic properties (coercive force, magnetization), and electrical conductivity were investigated. Annealing was carried out in a vacuum of 10^{-5} Torr in a magnetic field $H \sim 10^3$ Oe.

Because of specific features of the given technology, no $SmCo_5$ phase is present in the samples synthesized, which is a result of the high chemical activity of samarium particles: at the working vacuum used, their oxidation occurs. The Auger-analysis data have shown a significant content of carbon in the films. By electron-microscopic and X-ray diffraction, it was established that the structure of the films represents magnetic particles of a Co(C) solid solution with a size $D \sim 1.5$ nm surrounded by the samarium oxide with a volume of the magnetic phase ~60% [10]. The films have high electrical resistivity (ρ ~ 0.05 Ω cm) and high saturation magnetization ($M_s \approx 300$ G) but exhibit a superparamagnetic behavior (blocking temperature $T_b \approx 80$ K).

In Fig. 2a, curves of magnetization reversal in the plane of the film (curve *1*) and perpendicular to it (curve *2*), as well as hysteresis loops (Fig. 2b) for the films annealed at $T = 530$ K are presented. Measurements have been performed at room temperature. Electron-microscopic studies have shown that at such an annealing no real

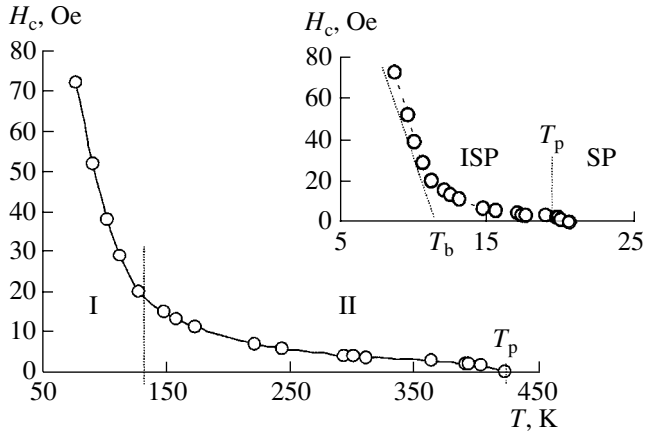

Fig. 3. Temperature dependence of the coercive force. The inset shows the $H_c = f(T^{1/2})$ dependence.

increase in the particle size occurs. It is seen that the magnetization-reversal curve *2* in the direction normal to the plane practically remains without a modification. This allows us to suggest that the saturation magnetization also practically did not change. At the same time, variations of the magnetic properties are observed upon the magnetization reversal in the plane of the sample (curve *1*). The film becomes ferromagnetic and the hysteresis loop ($H_c < 3$ Oe) appears already at $T = 300$ K. Besides, a uniaxial anisotropy is formed in the film ($H_K > 10$ Oe).

To analyze these variations of the magnetic properties in annealed films, we consider the temperature dependence of the coercive force (Fig. 3). In this dependence, it is possible to distinguish two regions: a sharp reduction of H_c with increasing T is observed in the region of low temperatures (region I); this dependence is less pronounced in the region of high temperatures, and the coercive force is equal to 0 at $T = T_p$ (region II).

For the interpretation of the $H_c(T)$ dependence, we use the phase diagram of the magnetic states offered in [8] for the ensemble of superparamagnetic particles. According to this diagram, the observed $H_c(T)$ curve can be connected with the transition of the system from the ferromagnetic blocked SP state (region I) into the region of magnetic ordering caused by the effects of magnetic interaction between nanoparticles (region II). In this region, instead of the usual transition from the ferromagnetic into the superparamagnetic state with increasing temperature, an intermediate region of magnetic ordering appears in the ensemble of superparamagnetic particles (ISP) in which just the interesting magnetic properties (for example, small H_c) are observed. In this case, another critical temperature—temperature of the transition into a superparamagnetic state (T_p)—takes place besides the blocking temperature.

The blocking temperature can be determined using the well-known expression [11] $H_c = H_{Co}[1 - (T/T_b)^{1/2}]$. The $H_c = f(T^{1/2})$ dependence is presented in the inset in Fig. 3.

The values of the magnetic and electrical properties can insignificantly vary depending on the conditions of synthesis and annealing. The data for the films in the initial condition and after annealing are listed in the table. It is seen that the annealed films have quite good soft magnetic properties and a high electrical resistivity.

Parameters of magnetic and electrical properties in Co–Sm–O films before and after annealing

	M, G	H_c, Oe ($T = 300$ K)	H_K, Oe ($T = 300$ K)	ρ, Ω cm
Initial	~300	–	–	5×10^{-2}
After annealing	~360	0.5–3.0	10–25	4.4×10^{-2}

4. CONCLUSIONS

Thus, instead of the usually accepted method of preparation of soft magnetic nanocrystalline materials using the structural transition from the amorphous into a nanocrystalline state [3], we offer using the magnetic transition inside nanogranular composites from a superparamagnetic state into the region of cooperative magnetic ordering caused by magnetic interactions between nanoparticles. In these materials, a greater electrical resistivity can be obtained, which makes them promising for using in microwave devices.

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