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Magnetic Interaction between Superparamagnetic Particles in Nanogranular Cobalt Films

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Abstract—A system of cobalt nanoparticles exhibits a transition from the superparamagnetic state into the state with cooperative magnetic ordering caused by the magnetic interaction between Co particles. It is shown that this transition can be used for obtaining nanogranular materials possessing soft magnetic properties at a large electric resistivity. *© 2004 MAIK "Nauka/Interperiodica".*

The magnetic properties of ferromagnetic (FM) nanoparticles (with diameters not exceeding 10 nm) are determined by a combination of characteristic dimensional effects: first, by the transition of particles into a monodomain state, whereby the particle size is comparable with the correlation length of exchange interaction; second, by the structural transformation accompanied either by a change in the phase state or by the formation of a complex nanostructural system comprising a "core" and a passivating "shell;" third, by the transition of the system of monodomain FM nanoparticles into a superparamagnetic state, whereby thermal fluctuations exceed the remagnetization threshold determined by the magnetic anisotropy. In other words, above a certain temperature (called the blocking temperature T_B), the ensemble of monodomain particles behaves like a gas of paramagnetic molecules possessing large magnetic moments.

In the class of nanocrystalline magnetic materials, a special position is occupied by granular nanocomposites comprising magnetic nanoparticles dispersed in a nonmagnetic matrix. Both the practical value and basic significance of such materials are determined by the fact that their magnetic properties can be controlled by varying the size and density of magnetic nanoparticles. An important role in the modification of magnetic properties of these systems is played by the magnetic interaction between particles.

Investigations of the magnetic properties of granulated systems [1–3] showed magnetic hysteresis at temperatures above the blocking temperature ($T > T_B$). This hysteresis is related to the magnetic interaction between nanoparticles, which otherwise would exhibit a purely superparamagnetic behavior. The transition from a superparamagnetic state into the state with a cooperative magnetic ordering caused by the magnetic interaction was theoretically and experimentally studied for composite materials with a magnetic phase content not exceeding 20 vol % [4–7]. However, interpretation of the magnetic properties of such systems is hindered by their complex dependence on many parameters and factors, including the dispersion of particle dimensions, the existence of various structural and magnetic phases in nanoparticles, the presence of a specific local anisotropy of nanoparticles, and the aforementioned magnetic interaction between nanoparticles. It is very difficult to establish with confidence which of these factors plays a decisive role in the formation of magnetic properties of such granular systems.

From the standpoint of practical applications, it would be of interest to study the magnetic properties of a system with a large volume fraction ($v > 40\%$) of the magnetic phase [8]. In such cases, the integral magnetic properties can be interpreted assuming a dominating role of the magnetic interaction between FM nanoparticles.

This letter presents the results of investigation of nanogranular films prepared by pulsed plasma sputtering of a $SmCo_5$ target in vacuum at a residual pressure of 10^{-6} Torr [9]. The thickness of the sample films was ~100 nm. Using these samples, we studied the effect of annealing on the structure, magnetic properties (coercive force, magnetization), and electric conductivity of nanogranular layers. The samples were annealed in vacuum at a pressure of 10^{-5} Torr with applied magnetic field of $H \sim 10^3$ Oe.

An important peculiarity of the employed technology is that the $SmCo_5$ phase is absent in the synthesized layers. This is explained by a high activity of sputtered samarium particles, which exhibit rapid oxidation in the residual atmosphere of the vacuum chamber. The data of Auger electron spectroscopy (AES) showed evidence of a considerable amount of carbon in the samples. The results of electron microscopy and X-ray diffraction measurements showed that the sample film structure comprises magnetic particles of a Co(C) solid solution with an average size of $D = 1.5$ nm surrounded

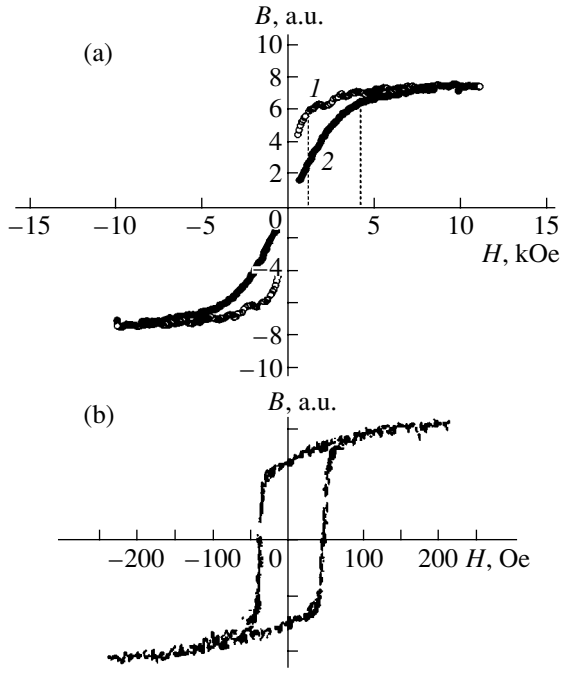

Fig. 1. Magnetization of the nanogranular films in the initial state: (a) room-temperature magnetization in the magnetic field oriented (*1*) in the sample plane and (*2*) in the perpendicular direction; (b) hysteresis loop observed at $T = 77$ K.

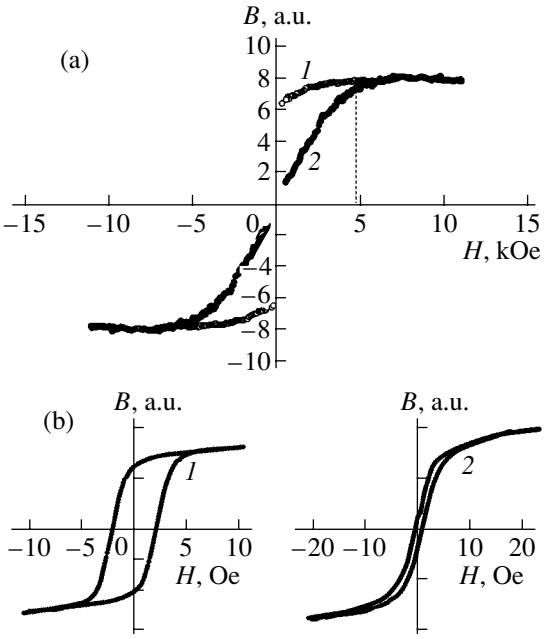

Fig. 2. Magnetization of the nanogranular films upon annealing at $T_{an} = 530$ K: (a) room-temperature magnetization in the magnetic field oriented (*1*) in the sample plane and (*2*) in the perpendicular direction; (b) hysteresis loops observed at room temperature in the directions of the (*1*) easy and (*2*) hard magnetization axis.

by samarium oxide (Sm_2O_3); the volume fraction of the magnetic phase amounted to ~60% [10]. Evidently, this morphology accounts for the relatively high resistivity of the samples ($\rho \sim 5 \times 10^{-2}$ Ω cm).

Figure 1a presents the magnetization curves measured at $T = 300$ K in the film plane (curve *1*) and in the perpendicular direction (curve *2*). Figure 1b shows the results of measurements at $T = 77$ K, which reveal a hysteresis loop. At room temperature, the magnetization curves exhibited no hysteresis, which was observed only at low temperatures ($T < T_B$). This behavior of the hysteresis loop is characteristic of a superparamagnetic material. Previously [10], it was established that the magnetic moment in such films is oriented in the sample plane. Therefore, using curve *2* in Fig. 1, it was possible to evaluate the effective saturation magnetization (~300 G).

Figure 2 presents analogous data—magnetization curves (a) and hysteresis loops (b)—for a film annealed at $T_{an} = 530$ K. The electron-microscopic examination showed that annealing did not produce any visible increase in the particle size. As can be seen, the magnetization curve *2* measured in the direction perpendicular to the sample plane remained virtually unchanged. This result suggests that the saturation magnetization also remained the same. On the other hand, there is a significant change in magnetic properties measured in the sample plane (curve *1*): the film becomes ferromagnetic and exhibits hysteresis even at $T = 300$ K ($H_C \le 3$ Oe); in addition there is evidence of a uniaxial anisotropy ($H_K \ge 10$ Oe).

To explain these changes in magnetic properties of the annealed film, let us consider the temperature dependence of the coercive force H_C (Fig. 3). This curve reveals two regions. In the region of low temperatures, H_C exhibits a sharp decrease with increasing temperature T (region I). At high temperatures, H_C varies less sharply with the temperature (region II) and turns to zero at $T = T_P$.

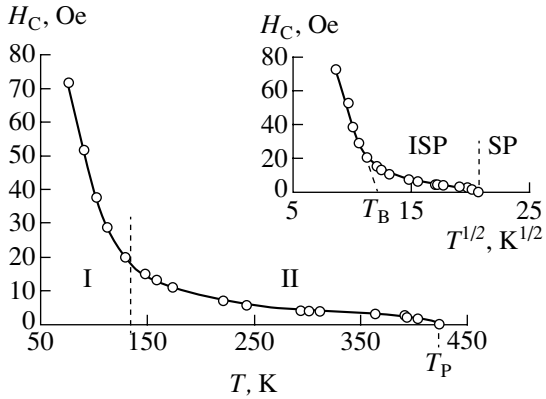

Fig. 3. Temperature dependence of the coercive force for a nanogranular film upon annealing. The inset shows the plot of $H_C = f(T^{1/2})$. See the text for explanations.

In order to interpret the behavior of $H_C = f(T)$, we use a phase diagram of the magnetic state of an ensemble of superparamagnetic particles proposed by Allia *et al.* [4]. According to this phase diagram, the $H_C = f(T)$ curve reflects the transition of our system from an FM-blocked superparamagnetic state (SP state, region I) to the state with magnetic ordering caused by the magnetic interaction between nanoparticles (region II). In the latter region, an increase in the temperature leads (instead of the usual transition from the FM to superparamagnetic state) to the appearance of an intermediate magnetically ordered state in the ensemble of superparamagnetic particles (ISP state, region II), where the material exhibits unusual magnetic properties (e.g., small coercive force H_C). In addition to the blocking temperature, the material is characterized by another critical temperature: the temperature of transition to the superparamagnetic state (T_P).

The blocking temperature can be estimated using the well-known relationship

$$H_C = H_{C0}[1 - (T/T_B)^{1/2}] \quad (1)$$

and the plot of $H_C = f(T^{1/2})$ presented in the inset in Fig. 3. The blocking temperature determined from these data is $T_B \sim 130$ K. In the interval $T_P > T > T_B$, the coercive force has a nonzero value, which is indicative of the existence of a magnetic order (region II). The magnetic energy of the ensemble of interacting magnetic nanoparticles can be expressed as [5]

$$E = KV + K_m M^2, \quad (2)$$

where K is the anisotropy constant, V is the particle volume, M is the magnetization, and K_m is the magnetic interaction constant. The system exhibits a transition to the superparamagnetic state ($H_C = 0$) at

$$T_P = K_m M^2/3k_B, \quad (3)$$

where k_B is the Boltzman constant. As can be seen from Fig. 3, in our samples, $T_P \sim 450$ K.

The magnetic and electrical properties of the samples exhibit insignificant variations depending on the conditions of synthesis and annealing. Data for the films in the initial (as-grown) state and upon annealing are presented in the table. As can be seen, the annealed films exhibit soft magnetic properties at a relatively high electric resistivity.

Thus, instead of the traditional method of obtaining magnetically soft nanocrystalline materials by means of a structural transition from the amorphous to nanocrystalline state [12], we suggest using the magnetic transition in nanogranular composites from superparamagnetic state to the state with a cooperative magnetic ordering caused by the magnetic interaction between nanoparticles. Using this method, it is possible to obtain materials with increased electric resistivity, having good prospects for use in microwave devices.

Magnetic and electrical properties of Co–Sm–O films before and after annealing

Sample	M, G	H_C, Oe (T = 300 K)	H_k, Oe (T = 300 K)	ρ, Ω cm
Initial	~300	–	–	5×10^{-2}
Annealed	~360	0.5–3	10–25	4.3×10^{-2}

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