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LATTICE DYNAMICS  
AND PHASE TRANSITIONS

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## Temperature Effect on Structural Transformations in Nanocrystalline Cobalt Films

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**Abstract**—The effect of annealing temperature on the structure and magnetic properties of nanocrystalline cobalt films has been studied by nuclear magnetic resonance (NMR) and magnetometric (vibrational magnetometer) techniques. Interpretation of the experimental data demonstrates that the initial films have an amorphous-like structure due to the high degree of disordering in the intergranular regions and nanoparticles. This structure transforms into the equilibrium polycrystalline state through the formation of a number of intermediate phases. © 2000 MAIK “Nauka/Interperiodica”.

Considerable current interest has been expressed by researchers in nanophase materials—three-dimensional analogs of multilayer structures [1]. These materials possess unusual physical properties owing to the occurrence of new solid states [2]. An example of such materials is provided by nanocrystalline 3d metal films prepared by the pulsed plasma deposition [3–6]. The specific features of the pulsed deposition technique are the high pulsed condensation rate ( $\sim 10^5$  A/s) at a pulse length of  $\sim 10^{-4}$  s and at a pulse-duration ratio of  $\sim 10^3$ – $10^4$ , and the high cooling rate of condensate ( $\sim 10^8$  K/s) [5]. The films produced in these technological conditions and under a vacuum of  $10^{-6}$  torr are built up of 3d metal nanocrystallites ( $\leq 4$  nm in size) surrounded by a carbon “coating” [6].

The novelty of the method resides in the fact that the limiting dispersion of crystal structure in the chosen direction is achieved at superhigh condensation rates when the number of arising nuclei is so great that the radius of a critical nucleus coincides with the coalescence radius. On the other hand, the high surface reactivity of nanocrystallites formed under plasma deposition conditions and the large pulse-duration ratio cause the condensate to entrap a large amount of impurity atoms (predominantly, carbon) of residual gases in a vacuum chamber.

Analysis of the available data on the magnetic, electrical, structural, and spectral properties of iron films produced under the given technological conditions [3, 6] suggests that the central region of structural nanoblocks consists predominantly of the phase of supersaturated carbon solution in  $\alpha$ -Fe. However, for the cobalt films, this question remains unclear. The point is that the carbon content in the cobalt films is higher than that in the iron films (30 and 20 at. % C, respectively). At the same time, it is known from the data available in the

literature that an increase in the carbon content in nanogranular cobalt films leads to a change in the phase composition of the central region of structural blocks; that is, the hexagonal close-packed cobalt phase transforms into the  $\text{Co}_3\text{C}$  phase [7, 8]. Therefore, in order to interpret the unusual properties of nanocrystalline cobalt films, it is necessary to elucidate in detail their initial structure.

In the present work, the effect of annealing temperature on the structure and magnetic properties of cobalt films prepared by the pulsed plasma deposition was studied with the nuclear magnetic resonance (NMR) and magnetometric (vibrational magnetometer) techniques. As is known, the magnitude and distribution of the hyperfine nucleus field in magnetically ordered materials are proportional to the magnetization and carry information on the local electronic and chemical environment of atoms. Therefore, analysis of the NMR spectra makes it possible to elucidate the structure of the studied samples in detail.

The thickness of films deposited onto glass and silicon substrates was equal to 50–100 nm. The samples were subjected to multistage annealing under a vacuum of  $10^{-5}$  torr for 1 h at each fixed temperature  $T_{an}$ . The NMR spectra were obtained using the standard spin-echo two-pulse sequence at room temperature.

The NMR spectrum of the initial film is displayed in Fig. 1 (spectrum *a*). It can be seen that the NMR signal is a smeared peak centered at frequency  $f \sim 190$  MHz with a width of  $\sim 50$  MHz. Upon heating of the sample up to  $T_{an} = 400$ – $500$  K, the spectrum drastically changes. The resonance peak shifts toward the high-frequency range, and its maximum is observed at  $f = 215$  MHz. At  $T_{an} \sim 400$  K, the spectrum involves a long “tail” on the left edge of the line (Fig. 1, spectrum *b*). This tail contains several peaks whose location and

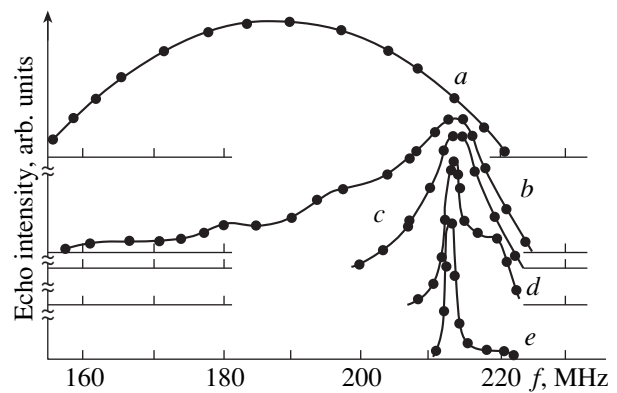
number vary from sample to sample and depend on the carbon content.

A further increase in the annealing temperature brings about the change in the line shape: a symmetric smeared peak (Fig. 1, spectrum *c*) transforms into a narrow peak at  $f = 213$  MHz and a “shoulder” in the frequency range 214–221 MHz (Fig. 1, spectrum *d*). At  $T_{an} = 700$  K, the peak becomes even narrower without change in the resonance frequency, and the intensity of the shoulder decreases (Fig. 1, spectrum *e*).

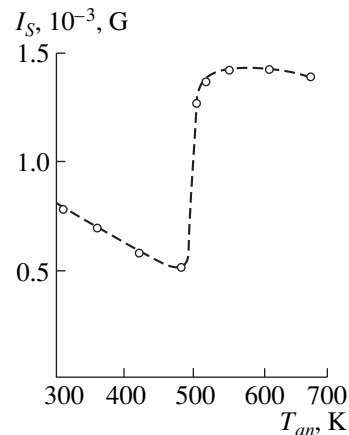
Figure 2 depicts the dependence of the magnetization  $I_s$  on the annealing temperature for the nanocrystalline cobalt film. The magnetization of the initial film is equal to approximately 850 G, which is considerably less than the magnetization of bulk cobalt samples. The annealing at temperature  $T_{an} \leq 550$  K leads to a further decrease in the magnetization  $I_s$ , whereas, upon annealing at  $T_{an} \geq 600$  K, the magnetization increases and virtually reaches the magnitude characteristic of bulk cobalt samples.

Let us consider the experimental data presented in Figs. 1 and 2. The change in the NMR spectra upon annealing of our films qualitatively follows a similar dependence obtained for the cobalt–phosphorus amorphous alloys in [9, 10]. The authors of these works observed the broadening of the NMR line and its shift toward the low-frequency range for amorphous cobalt ribbons and films. A decrease in the NMR frequency and, correspondingly, a decrease in the hyperfine field at cobalt nuclei was accounted for by the electron transfer from phosphorus ions to cobalt ions. According to the X-ray diffraction analysis, our samples consist of nanocrystallites less than 4 nm in size. As follows from the Auger spectroscopic data, these samples contain as much as 30 at. % C. It is assumed that the very broadened NMR spectra of the initial films indicate a high degree of structural disordering, which is determined not only by the intergranular graphite-like regions and a large ratio between the numbers of surface cobalt and bulk cobalt atoms, but also by the disordering of carbon ions dissolved in the cobalt nanoparticles. The latter assumption is confirmed by the presence of satellites in the NMR spectrum of the film after the first annealing. The number of satellites corresponds to the number of carbon ions in the nearest environment of each cobalt ion. This spread in the atomic configurations is responsible for the shape of the spectra of the initial films, which is similar to the shape of the spectra of cobalt–phosphorus amorphous materials.

A similar unusual combination of amorphism and nanocrystallinity was described by Delaunay *et al.* [11]. In this work, the microstructure of granular films prepared by the joint sputtering of cobalt and carbon was investigated at different carbon concentrations and different temperatures of substrate. It was found that the samples containing 27 at. % C are composed of cobalt nanoparticles (~5 nm in diameter) separated by carbon interlayers. However, these authors failed to



**Fig. 1.** NMR spectra of cobalt films prepared by pulsed plasma deposition: (a) initial film and films annealed at  $T_{an} =$  (b) 400, (c) 500, (d) 600, and (e) 700 K.



**Fig. 2.** Dependence of the magnetization  $I_s$  on the annealing temperature  $T_{an}$  for the nanocrystalline cobalt film.

determine the structure of nanoparticles even with the high-resolution electron microscopy, and, hence, the structure of nanoparticles was interpreted as an amorphous-like structure.

Upon heating of the films up to  $T_{an} = 400$ – $500$  K, carbon is likely to be displaced from the cobalt nanoparticles, and the resonance peak shifts toward the high-frequency range (Fig. 1; spectra *b*, *c*). The NMR signal in the cobalt–phosphorus polycrystalline films is observed at the same frequencies [10]. At room temperature, this signal is a superposition of two resonance lines, which correspond to the face-centered cubic (fcc) and hexagonal close-packed (hcp) phases of cobalt ( $f_1 = 213$  MHz and  $f_2 = 221$  MHz, respectively). A long tail appeared on the left edge of the NMR line after the first annealing (Fig. 1, spectrum *b*) can be associated with an incomplete displacement of carbon from the cobalt nanoparticles because of low temperature.

The formation of the hcp and fcc magnetic cobalt phases (Fig. 1, spectrum *c*) should seemingly lead to an

increase in the magnetization of samples. However, as is seen from Fig. 2, the value of  $I_s$  decreases almost by a factor of 1.5 compared to the magnetization of the initial film. This contradiction can be also explained with the results obtained by Delaunay *et al.* [11], who demonstrated that nanoparticles containing a mixture of the  $\text{Co}_2\text{C}$  and hcp Co phases are formed in the granular cobalt films prepared by the joint sputtering with carbon at the substrate temperature  $T = 470$  K. In [11], it was inferred that the carbide compound is formed just at  $T = 470$  K. Since the  $\text{Co}_2\text{C}$  phase does not exhibit magnetic properties at room temperature, its formation should cause the overall magnetization to decrease.

At  $T_{an} > 600$  K, the NMR line shape changes in the same frequency range: there appears a narrow peak and a broad shoulder, which correspond to a well ordered fcc phase and severely disordered hcp phase of cobalt. According to [11], at  $T = 620$  K, the  $\text{Co}_2\text{C}$  phase undergoes decomposition into the hcp cobalt phase and graphite-like carbon. This should be attended by an increase in the magnetization of samples, which is actually observed in Fig. 2.

A further increase in the annealing temperature results in an increase in the amount of the fcc cobalt phase at the expense of a decrease in the content of the hcp cobalt phase (Fig. 1, spectrum *e*); in this case, the magnetization remains virtually constant.

Thus, the investigation into the structure of nanocrystalline cobalt films by the NMR method demonstrated that the initial films consist of the cobalt particles with incorporated carbon atoms. The annealing at  $T_{an} > 550$  K results in the formation of a mixture composed of the hcp and fcc cobalt phases. A further increase in the annealing temperature leads to an

increase in the content of the fcc phase. The unusual temperature behavior of the magnetization is associated with the formation of the nonmagnetic cobalt carbide phase at  $T_{an} = 400$ – $500$  K and its decomposition at  $T_{an} > 550$  K.

## REFERENCES

1. R. W. Siegel, *Phys. Today* **10**, 46 (1993).
2. J. P. Perez, V. Dupuis, J. Tuaille, *et al.*, *J. Magn. Mater.* **145** (1–2), 74 (1995).
3. G. I. Frolov, V. S. Zhigalov, S. M. Zharkov, *et al.*, *Fiz. Tverd. Tela (S.-Peterburg)* **36** (4), 970 (1994).
4. G. I. Frolov, V. S. Zhigalov, A. I. Pol'skiĭ, *et al.*, *Fiz. Tverd. Tela (S.-Peterburg)* **38** (4), 1208 (1996).
5. V. S. Zhigalov, G. I. Frolov, and L. I. Kveglis, *Fiz. Tverd. Tela (S.-Peterburg)* **40** (11), 2074 (1998).
6. S. G. Ovchinnikov, B. A. Belyaev, I. S. Edelman, and G. I. Frolov, *Micron-Submicron Technologies for Magnetic Structures*, Preprint No. 776F IF SD RAN (Kirenskiĭ Inst. of Physics, Siberian Division, Russian Academy of Sciences) (1997).
7. Y. Saito, T. Yoshikawa, M. Okuda, *et al.*, *J. Appl. Phys.* **75** (1), 134 (1994).
8. Y. Yosida, S. Shida, T. Ohsuna, *et al.*, *J. Appl. Phys.* **76** (8), 4533 (1994).
9. K. Ray, J. Durand, J. I. Budnick, *et al.*, *J. Appl. Phys.* **49** (3), 1671 (1978).
10. V. K. Mal'tsev, G. I. Fish, and V. I. Tsifrinovich, *Fiz. Met. Metalloved.* **52** (2), 439 (1981).
11. J. J. Delaunay, T. Hayashi, M. Tomita, *et al.*, *J. Appl. Phys.* **82** (5), 2200 (1997).

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