

MAGNETIC PARTICLES
AND NANOCRYSTALLINE MATERIALS

Magnetic Properties of $\text{Ni}_x\text{Co}_{1-x}$ Nanoparticles
in Carbon Nanotubes¹

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Abstract—X-ray diffraction analysis, nuclear magnetic resonance, and low-temperature magnetic measurements were used to study the structure and magnetic parameters of nanoparticles $\text{Co}_{1-x}\text{Ni}_x$ ($x = 0\text{--}100$ at. %) located inside carbon nanotubes. It has been established that the behavior of the exchange constant versus alloy composition $A(x)$ is nonmonotonic. This fact is unexpected from the thermodynamic viewpoint and primary X-ray diffraction analysis, which show that only an fcc structure is characteristic of all $\text{Co}_{1-x}\text{Ni}_x$ particles. An analysis of structure defects using X-ray diffraction and NMR spectra explains the observed anomalies of magnetic properties as a result of the highly defect structure of ferromagnetic Co nanoparticles, which are formed as close-packed fcc structures with numerous stacking faults (layers of an hcp structure).

PACS numbers: 75.50.Tt, 81.07.De

DOI: 10.1134/S0031918X06140171

1. INTRODUCTION

The novel properties of magnetic nanoparticles are in focus of many fundamental research and practical applications [1, 2]. It is difficult to prevent metallic magnetic (Fe, Co, Ni) nanoparticles from oxidization under conventional experimental conditions. Several techniques, such as carbon encapsulation, reagent stabilizing, and passivation of nanoparticles, have been developed to protect metallic particles. The metallic particles in the carbon cages are believed to be a potential candidate for the high-density magnetic recording media.

To understand the properties of such particles, information on their structure and fundamental magnetic constants is needed. The fraction of subsurface atoms in nanoparticles is on the order of volume-atom fraction. Therefore, the excess surface energy in individual nanoparticles may result in the appearance of highly defect structures, and the physical properties of such particles should considerably differ from the properties of bulk materials.

The aim of this investigation is to determine the fundamental magnetic constants (exchange constant, spectral characteristics of nuclear magnetic resonance (NMR)) and the magnetostructural parameters (coercive force) in Co–Ni nanoparticles disposed inside carbon nanotubes. Our task was also the identification of

the atomic-structure peculiarities that affect the magnetic properties of our nanoparticles.

2. EXPERIMENTAL

The experimental methods used in this work are based on the features of both static magnetic parameters of individual ferromagnetic Co–Ni nanoparticles and their atomic and chemical structures. As a catalyst for synthesis of carbon nanotubes, nanoparticles of pure metals and alloys are used. The nanoparticles are formed by thermal decomposition of salts of the maleic acid ($\text{C}_6\text{H}_4(\text{COO})_2\text{Me}$ bimalates, where *Me* is a metal). To synthesize Ni–Co nanoparticles, metal solutions are mixed up in ratios 0:1, 2:8, 1:1, 8:2, 1:0 and dry.

The samples synthesized were characterized using scanning electron microscopy (SEM, JEOL ET 200), transmission electron microscopy (TEM, JEOL 100 C), and X-ray diffraction (XRD, DRON-SEIFERT-RM4). Static magnetic measurements were performed in a temperature range of 78–300 K in magnetic fields of up to 5 kOe using a vibrating-sample magnetometer. The contribution of the insert with an empty powder container was measured separately (it was ~1%) and subtracted from the results of measurements.

The temperature dependence of magnetization $M(T)$ of the nanoparticles was measured in a magnetic field $H = 3$ kOe. At low temperatures, the dependence is determined by thermal spin waves and is adequately described by the equation

$$M(T) = M_0(1 - BT^{3/2}). \quad (1)$$

¹ The text was submitted by the authors in English.

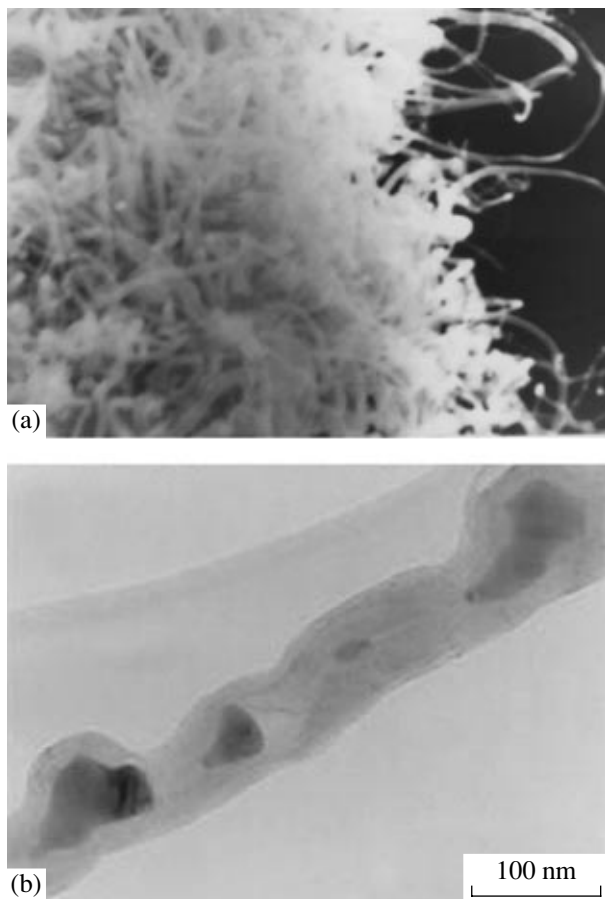


Fig. 1. Typical images of the samples obtained investigated by (a) SEM and (b) TEM.

This allows us to determine the Bloch constant B at the saturation magnetization from the experimental $M(T)$ dependences and to calculate the exchange interaction parameter A

$$A = \frac{k_B (g\mu_B)}{8\pi \left(\frac{M_0}{M_0}\right)^{1/3}} \left(\frac{2.612}{B}\right)^{2/3}, \quad (2)$$

where k_B is the Boltzmann constant, μ_B is the Bohr magneton, and g is the Lande factor.

Nuclear magnetic resonance (NMR) spectroscopy is very sensitive to the atomic structure of magnetic materials, since it records the chemical order in the first coordination shell. To determine the nearest-neighbor surroundings of Co atoms, the NMR spectra were measured by the spin-echo technique. The measurements were performed at room temperature in a frequency range of 150–230 MHz using a standard pulse spin-echo NMR spectrometer.

3. RESULTS AND DISCUSSION

Structure

The samples are powders of carbon nanotubes with an inner diameter of 10–50 nm partially filled with

metal. Figure 1 shows typical TEM images of individual nanotubes. Figure 1 makes evident the disposition of metal nanoparticles inside carbon nanotubes (dark regions in the micrographs of the nanotubes correspond to Co–Ni particles; semitransparent regions, to the carbon walls).

The diffraction patterns (Fig. 2) of the $\text{Co}_{1-x}\text{Ni}_x$ nanoparticles investigated suggest an isotropic nanocrystalline fcc structure of a Co–Ni solid solution. The identified reflections are indicated near the peaks in the figure. The conclusion that Co and Ni in the nanoparticles are in the solid-solution state results from good accordance of the lattice-parameter dependence on x to Vegard's law (see inset in Fig. 2). From the line widths of the reflections (111) and (222), we estimated, by the method described in [3], the grain size and the value of internal deformations. The results of this estimation are presented in Fig. 3. It is seen that the grain size and the level of internal deformations depend nonmonotonically on x . Furthermore, the $D(x)$ and $\epsilon(x)$ dependences correlate with each other.

Magnetism

The thermomagnetic curves $M(T)$ of the investigated powders of Co–Ni nanoparticles measured in an applied field of 3 kOe show that the values of the temperature gradients of magnetization do not exceed 2% in the range from 78 to 300 K and that the $M(T)$ dependences have a positive curvature. If there were an appreciable contribution from nanoparticles in the superparamagnetic state, the value of the temperature gradient would be equal to several tens percent and the $M(T)$ dependences be characterized by a negative curvature. This means that most nanoparticles are in the ferromagnetic state and their blocking temperature is considerably higher than room temperature. The value of the temperature gradients of magnetization of the investigated Co–Ni nanoparticles depends on their content. Bloch's constants were calculated from experimental $M(T)$ curves according to Eq. (1). To determine the value of the exchange constant, we used the magnetizations of bulk polycrystalline Co–Ni alloys. The value of A as a function of x also behaves nonmonotonically (see Fig. 4). An increase in x from 0.2 to 1 results in a decrease in A and when $x = 1$ the value of A is equal to that of bulk polycrystalline Ni. However, with transition to the Co nanoparticles ($x = 0$), it increases. The value of $A(x = 0)$ is less than $A(x = 0.2)$ and is considerably lower than it is for fcc Co.

Figure 5 displays the NMR spectrum of the Co nanoparticles investigated. The NMR spectrum of pure Co contains two main components corresponding to resonances at 213.5 MHz (fcc Co) and 221 MHz (hcp Co). The spectrum presented in Fig. 5 shows that the Co nanoparticles are mainly characterized by an fcc-type short-range ordering. In general, the NMR spectrum presented is described by the sum of two resonance lines; one corresponds to an fcc ordering of Co atoms

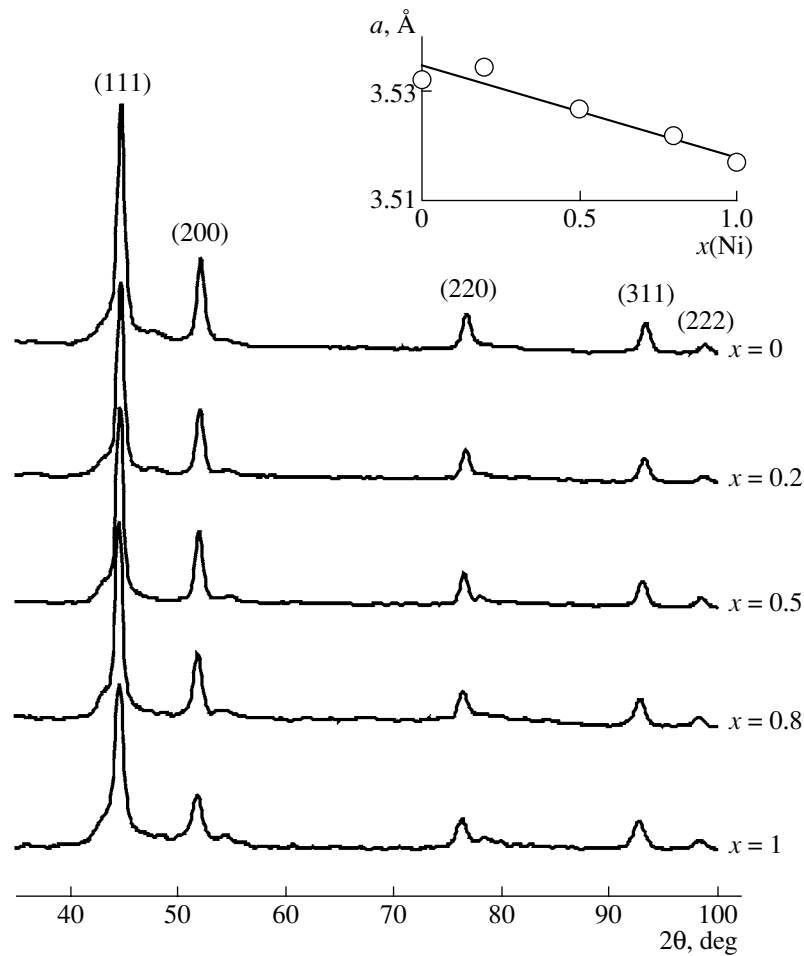


Fig. 2. Diffraction patterns of the $\text{Co}_{1-x}\text{Ni}_x$ nanoparticles investigated. In the inset, the dependence of the lattice parameter on x is given (solid line corresponds to Vegard's law).

(213.5 MHz), another (215.5 MHz), to Co atoms located at structural defects (stacking faults, see, e.g., [4]).

4. DISCUSSION

The nonmonotonic $A(x)$ dependence indicates the occurrence of some changes in the short range order in the nanoparticles investigated. It follows from X-ray diffraction data and from the literature that in Co nanoparticles with a size of 10–20 nm the only equilibrium structure is fcc. The correlation between the $D(x)$ and $\epsilon(x)$ dependences and the nonmonotonic $A(x)$ dependence are explained by the important role of stacking faults. The exchange-interaction parameters of the fcc and hcp polymorphic modifications of Co-based alloys are related as $A_{\text{fcc}}^{\text{Co}} \approx 2A_{\text{hcp}}^{\text{Co}}$ [5]. Here, fcc and hcp structures are both close-packed structures that are characterized by different sets of packing of the $(111)_{\text{fcc}}$ planes. The fcc structure is characterized by an ABCABC sequence of atomic layers, whereas for the hcp structure, an ABAB sequence is typical. Taking

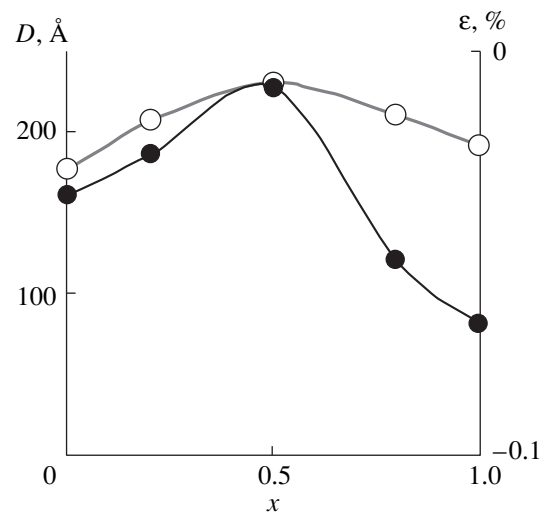


Fig. 3. Grain size D (empty circles) and internal deformations ϵ (solid circles) in the $\text{Co}_{1-x}\text{Ni}_x$ nanoparticles.

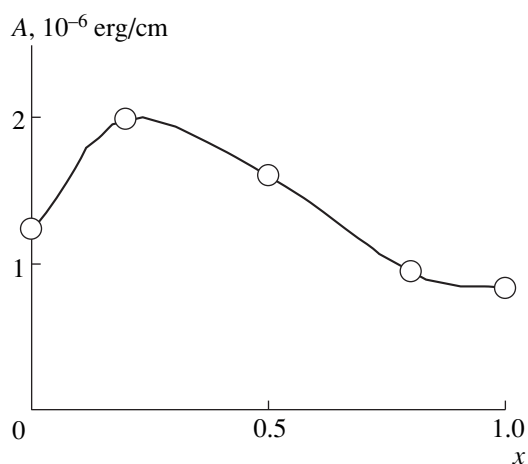


Fig. 4. The variation of the exchange constant (A) as a function of x for the $\text{Co}_{1-x}\text{Ni}_x$ nanoparticles.

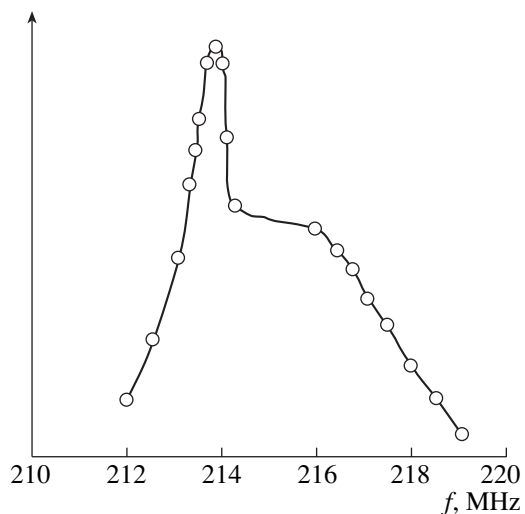


Fig. 5. NMR spectrum of the Co nanoparticles investigated.

into account this structural-defect correlation, the $D(x)$ and $\epsilon(x)$ dependences and the peculiarities of the NMR

spectrum become physically clear. Stacking faults can be considered as hcp defects. An increase in the number of such defects should result in a decrease in the value of A .

5. CONCLUSIONS

Thus, we established the structure and magnetic peculiarities of Co–Ni nanoparticles located inside carbon nanotubes. A reconcilable description of the peculiarities observed demands the consideration of nanoparticle structure as having an fcc structure with numerous stacking faults (layers with an hcp structure). This means that such materials are fundamentally nonequilibrium. Hence, equilibrium phase diagrams are inapplicable for the analysis of properties of nanoparticles of such alloys.

ACKNOWLEDGMENTS

This work was supported in part by the Krasnoyarsk Regional Science Foundation (project no. 12F0011C); Government Support of Young Russian Scientists (project no. MK-1684.2004.2); and Russian Foundation for Basic Research (project no. 04-02-16230).

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