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Fe Nanowires in Carbon Nanotubes as an Example of a One-Dimensional System of Exchange-Coupled Ferromagnetic Nanoparticles

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The cooperative phenomena revealed in the field and temperature dependences of the magnetization in a system of iron nanoparticles in carbon nanotubes were studied experimentally. The character of the temperature dependences of the magnetization indicates that the ferromagnetic Fe particles in carbon nanotubes are exchange-coupled. In the region where the magnetization approaches saturation, the magnetization curves reveal the power dependence $\Delta M \sim H^{-3/2}$ typical for a one-dimensional system of exchange-coupled ferromagnetic nanoparticles. © *2003 MAIK "Nauka/Interperiodica".*

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At present, many researchers are interested in the magnetic properties of ferromagnetic nanowires from the viewpoints of both possible applications and fundamental research [1–22]. Such effects as giant (70% [1], 20% [15]) and colossal (up to 10000% [2]) magnetoresistance and giant (as compared to bulk ferromagnets) coercive force (1–5 kOe) [1, 3–7, 17–19] have already been observed in magnetic nanowires.

Two methods are currently used for producing nanowire ensembles based on Fe, Co, Ni, and their alloys. The first method is the electrochemical deposition of a metal into cylindrical pores of such porous matrices as aluminum oxide [3–11], silicon [12], and polycarbonate membranes [13–16]. The second method is based on the arrangement of metal nanoparticles inside carbon nanotubes produced by the decomposition of compounds containing a magnetic 3D metal. This method uses chemical vapor deposition (CVD) [17–21] and carbon electric arc decomposition [2, 22].

Unusual magnetic properties of ferromagnetic nanoparticles are caused to a considerable extent by the cooperative effects in the magnetic system of strongly coupled nanoparticles. The cooperative effects in a system of exchange-coupled nanoparticles depend mainly on the strength of exchange coupling and the spatial arrangement of nanoparticles. In nanomaterials with a random distribution of the anisotropy axes of small particles, the main structural characteristics are the size of the nanoparticles and the dimensionality of their arrangement. As shown in [23], the average magnetic anisotropy (and, therefore, the coercive force H_c and the magnetic permeability) of such ferromagnetic nanomaterials is described by the power function $\langle K \rangle \sim K(R_c/\delta)^{2d/(4-d)}$, where K is the energy of the local magnetic anisotropy, R_c is the correlation radius of the random magnetic anisotropy (in nanocrystals R_c is usually taken to be half the grain size), $\delta = (A/K)^{1/2}$ is the exchange correlation length, A is the exchange interaction constant, and d is the dimensionality of the grain arrangement. It was shown in [23, 24] that the approach of the magnetization to saturation in ferromagnetic nanomaterials with $R_c < \delta$ (such materials can be considered as systems of exchange-coupled nanoparticles) is determined by the dimensionality d of the arrangement of nanoparticles. According to [23, 24], the reversible part of the magnetization curve of such ferromagnetic nanomaterials in fields $H < H_{ex} = 2A/MR_c^2$ (so-called exchange field) is described by the following formula:

$$\frac{M(H) - M_s}{M_s} = -\left(\frac{D^{1/2}H_a}{H_{ex}}\right)^2\left(\frac{H_{ex}}{H}\right)^{(4-d)/2}, \qquad (1)$$

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where $H_a = 2K/M_s$ is the local anisotropy field. Therefore, studies of the magnetization curves in the region where the magnetization approaches saturation combined with the study of the low-temperature dependence of the magnetization make it possible to obtain information about the parameters A, K, R_c, and d. In principle, these parameters could also be determined by studying the dependence of H_c on R_c, but this method is very laborious and methodologically difficult.

The goal of this work was to study experimentally the cooperative effects that are revealed in the field and temperature dependences of the magnetization of a system of iron nanoparticles in carbon nanotubes.

Experiment. Samples of two types were studied: samples $s1$ synthesized by the electric arc decomposition of $Fe(CO)_5$ [22] and samples $s2$ synthesized by the thermolysis of a mixture of C_{60} fullerene with ferrocene [21]. The samples were obtained in the form of powder consisting of carbon nanotubes filled with iron. Microphotographs of the nanotubes obtained by transmission electron microscopy (TEM) are shown in Fig. 1. It can be seen that the inner cavities of the nanotubes are partially filled with iron (dark regions in the microphotographs of the nanotubes correspond to Fe particles; semitransparent regions, to the carbon walls). The weight fraction of Fe in the nanocomposites under consideration was estimated from the magnetization measurement results: in $s1$ it was ~50–60%; in $s2$, ~15–25%. It can also be seen in Fig. 1 that the nanotubes constituting powder samples $s1$ and $s2$ differ in their morphology: $s1$ consists of distorted nanotubes (Fig. 1a), whereas $s2$ is composed of straight-wall nanotubes (Fig. 1b). The nanotubes of both $s1$ and $s2$ types have a characteristic inner diameter of ~100 Å. Scanning electron microscopy showed that the average length of the nanotubes of both types was ~10 μm [21, 22]. X-ray diffraction studies and Mössbauer spectroscopy showed that the nanowires inside the nanotubes consisted of α-Fe and Fe_3C magnetic particles [21, 22].

Magnetic measurements were performed using a vibrating-sample magnetometer with a superconducting solenoid in fields of up to 60 kOe and in the temperature range 4.2 to 200 K. The contribution of the insert with an empty powder container was measured separately (it was ~1%) and subtracted from the results of measurement.

Results and discussion. The low-temperature magnetization curves for samples $s1$ and $s2$ are shown in Fig. 2. These curves $M(T)$ were measured in the external field $H = 20$ kOe within the temperature range 4.2 to 200 K. It can be seen that the curves do not exhibit singularities typical for superparamagnetic particles, which means that the small Fe particles inside the carbon nanotubes are exchange-coupled.

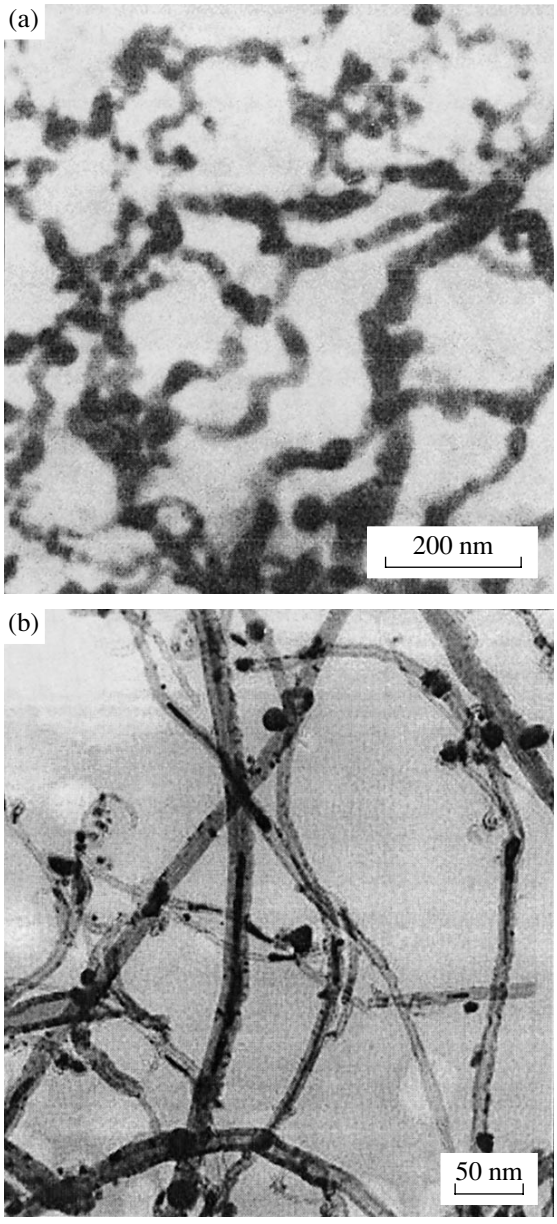

Fig. 1. (a) TEM image of iron-filled carbon nanotubes synthesized by electric arc decomposition of $Fe(CO)_5$ [22]; (b) TEM image of iron-filled carbon nanotubes synthesized by thermolysis of a mixture of C_{60} fullerene with ferrocene [21].

The experimental dependences $M(T)/M(0)$ are well described by the theoretical expression known as the Bloch law (solid lines in Fig. 2):

$$M_s(T) = M_{s0}(1 - BT^{3/2} - CT^{5/2}). \quad (2)$$

The relation of the coefficients B and C in Eq. (2) with the main magnetic constants of the material (exchange interaction constant A and the mean length $\langle r^2 \rangle^{1/2}$ of the atomic exchange coupling) is described

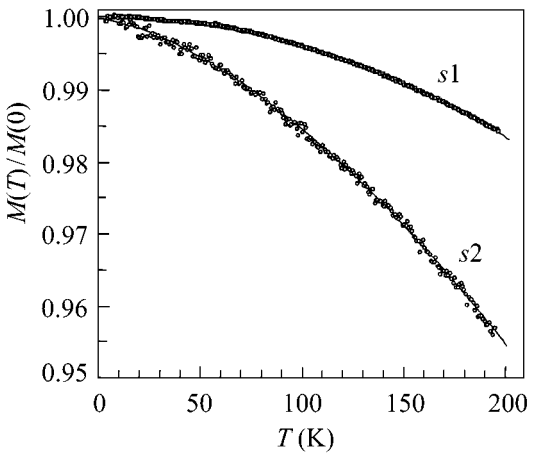

Fig. 2. Normalized magnetization $M(T)/M(0)$ as a function of temperature in an external field H = 20 kOe for Fe nanowires in carbon nanotubes.

by the well-known formulas

$$A = \frac{k}{8\pi}\left(\frac{g\mu_B}{M_{s0}}\right)^{1/3}\left(\frac{2.612}{B}\right)^{2/3}, \quad (3)$$

$$\langle r^2\rangle \equiv \sum_{ij} J_{ij} r_{ij}^4 / \sum_{ij} J_{ij} r_{ij}^2 = \frac{1.57}{\pi}\frac{C}{B^{5/3}}\left(\frac{g\mu_B}{M_{s0}}\right)^{2/3}, \quad (4)$$

where J_{ij} is the exchange integral for a pair of neighboring spins in the atomic lattice r_{ij}.

The calculated constants B, C, A, and $\langle r^2\rangle^{1/2}$ for the Fe nanowires under consideration are given in the table together with the well-known values of the same constants for an α-Fe crystal and a cementite (Fe_3C) crystal.

The measured magnetization curves of the Fe nanowires under consideration are shown in Fig. 3 both as standard isotherms $M(H)$ and as $\Delta M/M_s$ vs. $H^{-3/2}$ curves. The high-field curves of magnetization of the Fe nanowires plotted in coordinates $\Delta M/M_s$ vs. $H^{3/2}$ include rectilinear segments both at liquid helium temperature and at T = 200 K. These segments indicate that $\Delta M/M_s$ is proportional to $H^{-3/2}$ in a field range up to 60 kOe. The curves shown in Fig. 3 comply with Eq. (1). They indicate that the exponent of the power dependence describing the approach of the magnetization to saturation is independent of the temperature and the process of the synthesis of the ferromagnetic material under consideration, but depends only on the dimensionality d of the arrangement of the exchange-coupled grains. In the case under consideration, the dimensionality is 1.

Table

	(*s*1)	(*s*2)	α-Fe	Fe_3C
B, 10^{-5} K$^{-3/2}$	0.35	1.7	0.34	2.9
C, 10^{-8} K$^{-5/2}$	1.7	1.1	0.1	–
$\langle r^2\rangle^{1/2}$, Å	7	1.5	2	–
A, 10^{-6} erg/cm	2.0	0.75	2.1	0.49

The dependence $\Delta M/M_s \sim H^{-1/2}$ (d = 3) describing the approach of the magnetization to saturation in amorphous and nanocrystalline magnetic materials was predicted in [25] and experimentally obtained in [26]. It is well known to magnetologists and widely used for interpreting the experimental data on the approach of the magnetization to saturation in amorphous and nanocrystalline magnetic materials [27–32]. The dependence $\Delta M/M_s \sim H^{-1}$ (d = 2) has been recently observed in experiments with ultrathin nanocrystalline and amorphous Co layers [23]. The experimental curves of the Fe nanowire magnetization obtained in this work reveal the power dependence $\Delta M/M_s \sim H^{-3/2}$ typical for a one-dimensional chain of exchange-coupled ferromagnetic grains. It should be noted that the magnetic properties of such ferromagnetic nanowires are determined mainly by the specific structure of the spin system, which can be described as an ensemble of one-dimensional magnetic units [23, 27] or Imry–Ma domains [33]. Therefore, an increase in the coercive force H_c in nanowires in comparison with ferromagnetic films and bulk materials can be explained using the equation $\langle K\rangle = K/N^{1/2} = K(R_c/R_f)^{d/2}$ [23], where $2R_f$ is the magnetic unit size and N is the number of nanoparticles constituting a single magnetic unit. In nanostructured magnetic materials, the following relation is usually observed: $x = R_c/R_f < 1$ [23, 27]. Raising both sides of the relation to a power $d/2$, we find that, all other factors being the same, the result is the largest for d = 1 than for d = 3 or d = 2. This means that the effective anisotropy (and, therefore, the coercive force) is greater in one-dimensional exchange-coupled systems of ferromagnetic nanoparticles than in similar 2D and 3D systems.

It should be noted in conclusion that a number of papers have been published recently on the theoretical estimation and numerical simulation of the magnetization distribution and the magnetic properties of one-dimensional exchange-coupled nanosystems [34–38]. The results obtained in these papers can be applied to new magnetic systems, such as ferromagnetic nanowires (though with some reservations about the magnetodipole interaction, which is disregarded in these works). In particular, they can be used to interpret the

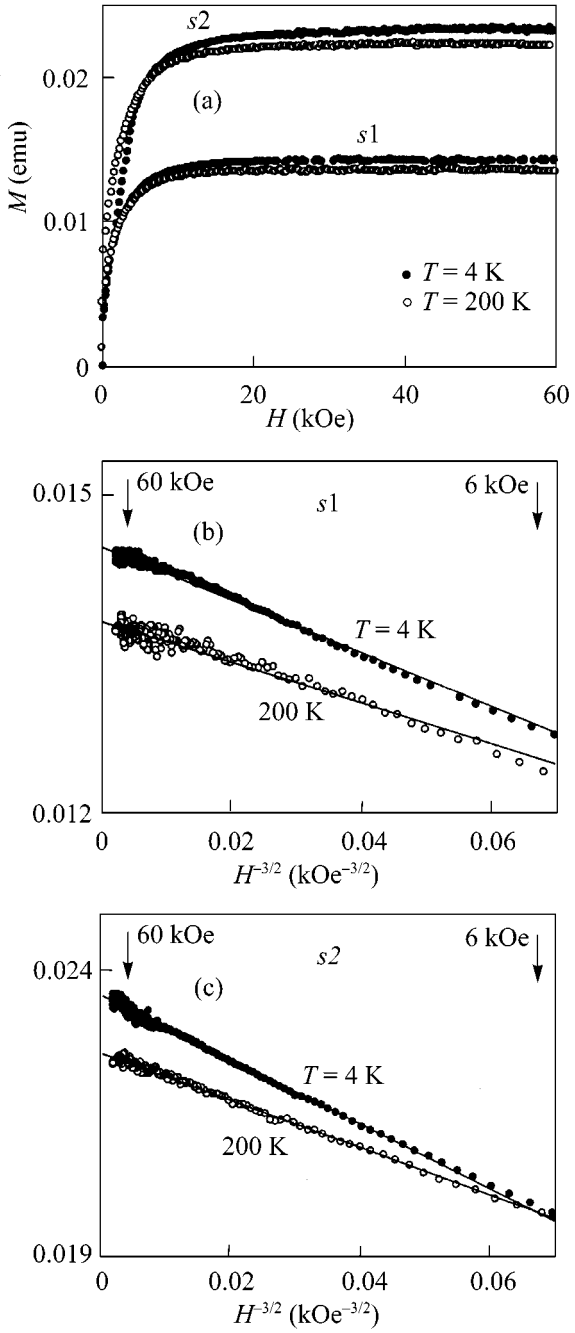

Fig. 3. (a) Curves of magnetization of Fe nanowires in carbon nanotubes; (b) high-field regions of the magnetization curves plotted in coordinates $\Delta M/M_s$ vs. $H^{-3/2}$ for sample *s*1; (c) the same for sample *s*2.

changes in some magnetic properties of nanowires through the changes in the main magnetic constants and structural parameters measured in the experiment.

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