*Technical Physics Letters, Vol. 31, No. 6, 2005, pp. 454–456. Translated from Pis'ma v Zhurnal Tekhnicheskoĭ Fiziki, Vol. 31, No. 11, 2005, pp. 12–18.*


# Magnetic Anisotropy in the Films of Oriented Carbon Nanotubes Filled with Iron Nanoparticles

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Received December 14, 2004

**Abstract**—Films of carbon nanotubes oriented perpendicularly to the substrate surface and filled with iron nanoparticles have been synthesized and studied. Morphological features of these nanocomposite films lead to the appearance of an easy magnetization axis, which is perpendicular to the film plane. A method for enhancement of this effect is suggested and successfully tested. © *2005 Pleiades Publishing, Inc.*

Carbon nanotubes (CNTs) have received much attention due to a unique combination of electronic and magnetic properties. These properties make CNTs a highly promising material for the creation of a new generation of devices, such as emission tubes, nanotransistors, sources of spin-polarized electrons, planar displays, and for the development of hydrogen storage systems [1]. One of the most attractive applications of CNTs, which is directly related to their annular morphology and extremely high aspect ratio, is their use as nanodimensional containers for the second phase, in particular, a magnetically ordered one [2]. The introduction of magnetic phases in CNTs may lead to promising results in view of a significant shape anisotropy that must influence the encapsulated material. For example, this may provide for a better stabilization of the magnetic order (with respect to thermal fluctuations) as compared to that achieved in systems of equiaxial magnetic nanoparticles. Additional interest in such composite materials is related to the basic aspects of magnetic ordering in nearly one-dimensional nanostructures [3].

From the standpoint of practical applications, CNTs filled with a ferromagnetic phase are of interest as a media with a coercive force $H_c$ exceeding theoretical predictions based on current knowledge about magneto-crystalline anisotropy ($H_c = 2K/M$) of bulk ferromagnetic materials. This possibility is related to the nanometer transverse dimensions of CNTs and to a significant influence of highly anisotropic interfaces on the magnetization processes. It is believed that the ability to control the magnetic anisotropy and coercivity of magnetic-phase-filled CNTs will lead to the development of new media for ultrahigh-density data recording, highly effective probes for magnetic force microscopes, and new recording heads [4].

This Letter reports the results of investigation of the magnetic anisotropy of a nanocomposite film comprising oriented CNTs filled with iron nanoparticles.

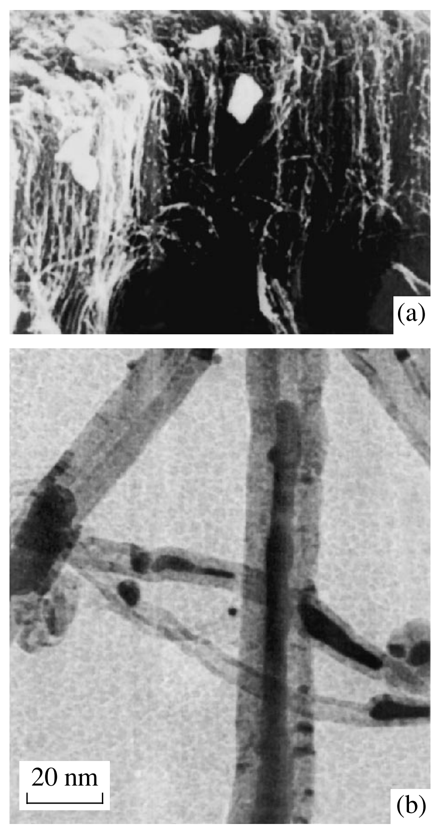


**Fig. 1.** (a) SEM image of a cleaved film composed of oriented CNTs; (b) TEM image of CNTs filled with Fe nanoparticles.

The films of oriented CNTs were obtained by thermolysis of a mixed vapor of $C_{60}$ fullerene (a source of carbon) and ferrocene (a source of iron and the catalyst). A mixture of fullerene $C_{60}$ and ferrocene (1 : 1) was placed into an alundum boat and transferred to a hot zone of the reactor. The duration of synthesis was 1 h. Upon cooling of the reactor, a dense black film was exfoliated from the inner surface of the quartz tube [5].

The thickness of exfoliated films was 10–15 μm. Examination by scanning electron microscopy (SEM) showed that the synthesized film comprises an agglomerate of nanotubes oriented parallel to each other, with a diameter of 10–20 nm and a length equal to or smaller than the film thickness (Fig. 1a). The SEM image of a cleaved section shows that the tubes are aligned predominantly perpendicularly to the substrate. Figure 1b presents an image obtained in the regime of transmission electron microscopy (TEM), from which it is seen that the inner cavities of CNTs are partly filled with iron (dark regions in the micrograph correspond to Fe particles and gray regions correspond to semitransparent graphite walls). Using the results of magnetization measurements, we determined the value of saturation magnetization and estimated the weight fraction of Fe atoms in the nanocomposite, which amounted to ~15–20%.

The macroscopic magnetic anisotropy of the obtained films was studied using a torque magnetometer. Figure 2 shows a plot of the torque versus the angle of the external magnetic field relative to the normal to the film surface. As can be seen from these data, the sample exhibits a pronounced uniaxial anisotropy, with the easy axis oriented perpendicularly to the film plane (that is, parallel to the direction of predominant orientation of CNTs). This anisotropy is apparently due to the anisotropy of Fe particles and the texture of nanotubes containing these particles.

The results of magnetization measurements using a vibrating sample magnetometer also provide information on the magnetic anisotropy in the system studied. However, the $M(H)$ curves of the nanocomposite films show only a weakly pronounced anisotropy with an easy axis perpendicular to the film surface (Fig. 3a). It was established that this result is explained by a nonideal texture and the lack of mechanical rigidity in the system of magnetic filaments. In order to enhance the texture and to impart rigidity to the agglomerate of CNTs filled with Fe nanoparticles, we fixed the orientation of nanotubes by placing the sample into a magnetic field oriented perpendicular to the film surface and impregnating the material with paraffin. Using this method, we obtained CNT film samples with a nonideal but well-pronounced magnetic anisotropy and the easy axis perpendicular to the film surface (Fig. 3b).

The energy of magnetic anisotropy was determined from the experimental magnetization curves and calculated using the formula

$$K_\perp = \int (M_\perp(H) - M_\parallel(H))dH.$$

Some typical estimates are presented in the table. The

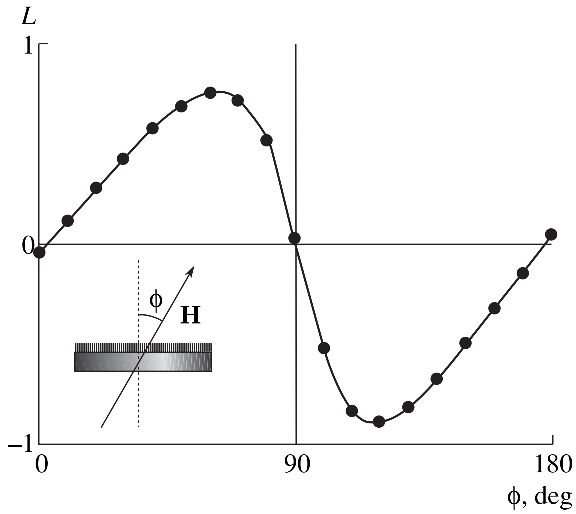


**Fig. 2.** A typical curve of the torque versus the angle of the external magnetic field relative to the normal to the film surface.

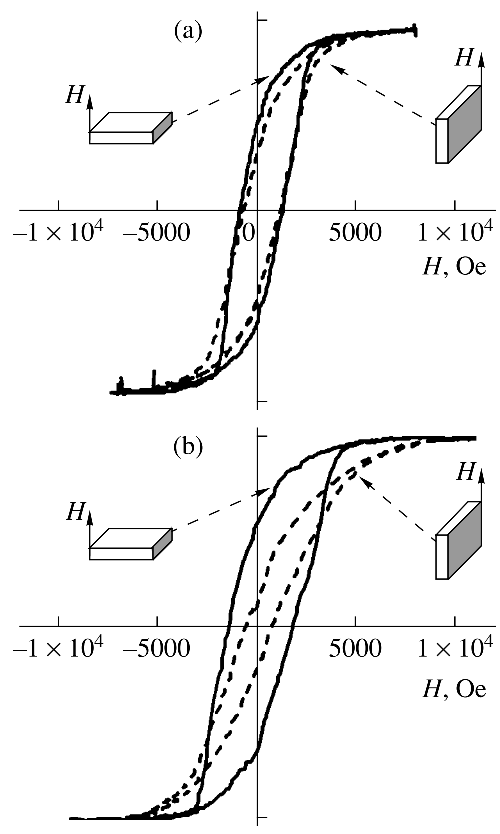


**Fig. 3.** Magnetization curves of a film composed of oriented CNTs filled with Fe nanoparticles, measured (a) in the initial state and (b) upon fixation of CNTs in a magnetic field of 3000 Oe.

The energy of magnetic anisotropy of a film of CNTs filled with Fe nanoparticles

| | Initial film | Film with CNTs fixed in magnetic field | |
|---|---|---|---|
| | | 500 Oe | 3000 Oe |
| $K_{\perp}$, $10^6$ erg/cm$^3$ | 0.9 | 1.6 | 2.8 |

maximum possible value of the energy of magnetic anisotropy for our nanocomposites modeled by cylindrical magnetic filaments can be evaluated as $\pi M_S^2 \sim 8 \times 10^6$ erg/cm$^3$. This implies that, by fixing the F-filled CNTs in a stronger magnetic field, we may provide for a threefold increase in the energy of magnetic anisotropy as compared to the maximum $K_{\perp}$ value achieved in our experiments. The nanocomposite film with the CNTs fixed in a field of 3000 Oe was also characterized by the energy of magnetic anisotropy determined from the $M_{\perp}(H)$ and $M_{\parallel}(H)$ curves measured at $T = 4.2$ K. The value of $K_{\perp}$ determined from these data was also equal to $2.8 \times 10^6$ erg/cm$^3$. The agreement of results obtained at room temperature and 4.2 K shows evidence for the same mechanism of magnetic anisotropy (shape anisotropy) and is indicative of an insignificant variation of the saturation magnetization of Fe nanoparticles in the entire temperature range from 4.2 to 300 K [3].

In order to evaluate a contribution due to the magnetocrystalline anisotropy to the observed macroscopic anisotropy, we measured the X-ray diffraction curves with and without the field. A comparison of the results of these measurements revealed no significant differences and showed the absence of a crystallographic texture. This implies that the crystallographic orientation of metal nanoparticles inside CNTs is virtually random and, on the average, is independent of the orientation of nanotubes. Therefore, the contribution due to the magnetocrystalline anisotropy is small compared to that due to the shape anisotropy of Fe nanoparticles contained inside the CNTs.

The coercive force of Fe particles reached 2000 Oe and 4.2 K and only slightly decreased (1800 Oe) upon increasing the temperature to 300 K. This result indicates that, despite small transverse dimensions of the CNTs, the blocking temperature $T_B$ (corresponding to the ferromagnet–superparamagnet transition) for the Fe particles inside CNTs is significantly higher than room temperature. The simplest estimate of the blocking temperature is provided by the formula $T_B \sim VK/k_B$, where $V \sim d^2 l$ is the average volume of a nanoparticle, $d$ is the average diameter of Fe filaments, $l$ is their length, $K$ is the energy of the local magnetic anisotropy, and $k_B$ is the Boltzmann constant. In our samples, an increase in $T_B$ is related to a considerable value of $V$ achieved due to a large aspect ratio ($l \gg d$) of the Fe nanoparticles.

**Acknowledgments.** This study was supported by the KKFN Foundation (project no. 12F0011C), the Russian Foundation for Basic Research (project no. 04-02-16230), and the Russian Science Support Foundation (project no. MK-1684.2004.2).

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*Translated by P. Pozdeev*