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Magnetic Properties of Nanocomposites Based on Magnetically Functionalized Carbon Nanotubes

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Introduction

Magnetic nanocomposites consisting of nanoparticles (NPs) of magnetic material dispersed in a solid matrix have received an increasing interest during last years because of their potential applications in magnetoelectronics and biomedicine [1]. New functionalities are obtained when combining a favorable matrix and filler properties [2]. However, it is still very important to understand the nature of magnetic interaction between NPs and the possible role of matrix which could influence the strength of this coupling. In particular, when the average distance between NPs is in the nanometric range, the exchange interaction could dominate. At that the magnetic anisotropy of each NP should also be taken into account, thus creating very complicated picture of interparticle magnetic interaction. Moreover, the interplay between the exchange interaction and magnetic anisotropy of ferromagnetic NPs intercalated into an appropriate matrix can be changed by varying their concentration, shape and size. Therefore, when the anisotropy dominates, magnetic moments of ferromagnetic NPs are aligned along their anisotropy axis giving a way to a disordered state [3]. In the opposite case, in the limit of weak anisotropy, the exchange interaction creates long range ferromagnetic order [4]. The matrix material could also induce additional difficulties in the experimental data interpretation. For example, for a nanocomposite consisting of carbon nanotubes (CNTs) with intercalated magnetic NPs, the CNT alignment [5] and/or possible indirect exchange coupling [6] could significantly modify the nanocomposite properties with respect to other matrix materials, like polymers [2], silica [7], porous silicon [8], etc.

Since the magnetic properties are expected to change significantly when the size at least in one direction is reduced below the single domain scale, a controllable procedure of NPs growth is of great importance. Generally, magnetic NPs smaller than 30 nm could be prepared by different methods, such as co-precipitation, thermal decomposition, emulsion method, hydrothermal synthesis [9], co-evaporation, co-sputtering [2], laser ablation in liquid [10], etc. On the other hand, it is necessary to precisely control the chemical stoichiometry of the NPs in the nanocomposite, their shape, as well as the average distance between them. From this viewpoint, CNT-based magnetic nanocomposites are very promising. Generally, CNTs are synthesized involving carbon decomposition of organic precursor over 3d catalytic metals like Fe, Ni, and Co [11]. At that the ferromagnetic catalytic nanoparticles could be intercalated over the whole volume of the sample and the magnetic CNT-based nanocomposite is synthesized *in situ*, during the CNTs growth. Such nanocomposites are proposed to be called as magnetically functionalized CNTs (MFCNTs) [12,13].

It is possible to produce aligned and macroscopically large CNT arrays filled with ferromagnetic NPs of different morphology and phase content [14,15]. Moreover, the ferromagnetic inclusions are covered by carbon shell thus preventing oxidation and accordingly some antiferromagnetic contribution [16]. Therefore, such MFCNTs possess high temperature stability. The coercivity of these nanocomposites is much larger with respect to bulk ferromagnets, reaching the values of thousands of Oersteds [17].

From a fundamental point of view, MFCNTs are interesting because carbon media by itself possess magnetic properties [18]. For example, the defectless carbon-based materials are basically diamagnetic, while by introducing defects in them one gets the paramagnetic behavior [19]. The walls of the graphitic layers encapsulating the metallic NP provide a magnetic separation between vicinal particles. As it has been shown, the diamagnetic susceptibility of an aligned array of CNT (diameter 10 nm) is very strong when the axis of the tubes is perpendicular to the applied magnetic field, this might decrease or even prevent the dipolar interactions between NPs [20]. At the same time, the indirect exchange coupling between magnetic NPs in CNT media could be of great importance for determining the entire magnetic properties [6]. Therefore, the magnetic properties of NPs are influenced by CNTs as a peculiar magnetic medium [21].

The aim of the present work is to find the correlation between the concentration, chemical stoichiometry and location of the ferromagnetic catalytic nanoparticles in MFCNTs, and its magnetic properties. Particular attention is given to the influence of the alignment of the CNT arrays on the interplay between the exchange coupling and magnetic anisotropy of nanoparticles. In particular, we analyze in details the correlation functions of the magnetic anisotropy axes which describe the magnetic state of iron-based NPs in CNT arrays and we explicitly show the dependence of the obtained correlation functions on such important technological parameter as the ferrocene content C_F in ferrocene/xylene solution during the floating catalyst chemical vapor deposition (CVD).

Samples Fabrication and Experimental Technique

Floating catalyst CVD was used for the synthesis of aligned MFCNTs. This low-cost, simple and effective technique offered the possibility to grow arrays of NPs with variable size and chemical state [11]. Indeed, various concentrations of ferrocene/xylene solution used as a feedstock for MFCNTs growth allowed obtaining arrays of aligned multi-wall CNTs on Si/SiO₂ substrates with different percentage content, shape, aspect ratio and chemical state of iron [22]. In particular, in this chapter we show the results for three concentrations of ferrocene Fe(C₅H₅)₂, $C_F = 0.5$ wt% (sample A), 1 wt% (sample B) and 10 wt% (sample C), respectively. The temperature in the reaction zone was fixed to 1150 K and the growth duration was 1 min. This created vertically-aligned MFCNT arrays of typical thickness of 50 – 100 μ m. In Fig. 9.1 we show the scanning electron microscopy (SEM) images of aligned MFCNT arrays synthesized for two ferrocene concentrations, $C_F = 0.5$ wt% and $C_F = 10$ wt%, respectively.

In this work, a lot of attention was given to the influence of the alignment of MFCNTs on their magnetic properties. For this purpose we measured also the magnetic properties of disaligned samples, which are powders, obtained from the aligned samples. SEM images of the disaligned (powder) MFCNTs are presented in Fig. 9.2. In a low resolution SEM image (× 500) (Fig. 9.2a) it is depicted that the composite represents disordered blocks of MFCNTs arrays. At a higher magnification (× 50000) (Fig. 9.2b) one can observe the morphology of a single block of a MFCNTs array representing the aligned CNTs.

The structure and composition of the aligned CNT arrays with intercalated iron-based NPs were investigated in details earlier by scanning and transmission electron microscopies, Raman, Mössbauer and X-ray photoemission spectroscopies (XPS), as well as by X-ray Θ -2 Θ diffraction. For C_F = 0.5wt% Febased nanoparticles are situated mostly inside nanotubes, while for $C_{\rm F}$ = 10wt% they are distributed over the whole array, intercalated also between CNTs [13,23]. In Fig. 9.3 we show the high resolution transmission electron microscopy (HRTEM) image of nanoparticles inside the CNT. Sample was synthesized with $C_{\rm F}$ = 0.5wt%. The single crystalline structure is well seen. The nanoparticle has a nearly spherical shape (i.e. the aspect ratio is close to 1) with a diameter of 10–15 nm. The nanoparticle displayed in Fig. 9.3b corresponds to a single Fe₃C nanoparticle. More details on observations and analyses of High Resolution TEM images are reported elsewhere [24]. Increasing of $C_{\rm F}$ leads to the formation of small ferromagnetic nanowires inside CNT together with spherical like nanoparticles on the walls and inside walls of CNT. At that the aspect ratio of small nanowires reaches the value of 20. The diameter of CNT also depends on the $C_{\rm F}$ content and changes from 5-30 nm for $C_{\rm F}$ = 0.5wt% to 50-70 nm for $C_{\rm F}$ = 10wt% [23]. It was also established that the major ferromagnetic phases were α -Fe and cementite Fe₃C [15,23]. Mössbauer spectroscopy showed that the content of the Fe₃C is increased with $C_{\rm F}$ growth. For $C_{\rm F}$ = 10% it reached the value of 80-90%. Reversely, content of α -Fe phase dropped with $C_{\rm F}$. Thus for $C_{\rm F}$ = 10% it became less than 15% [15]. XRD analysis did not reveal the presence of internal stresses at room temperature in our samples [22,23].



SEM images of aligned CNT arrays synthesized for two different ferrocene concentrations. (a) $C_F = 0.5$ wt%. (b) $C_F = 10$ wt%



FIGURE 9.2

SEM images of the disaligned MFCNT array (powder) at different magnifications: (a) (× 500) disordered blocks of MFCNTs arrays; (b) (× 50000) morphology of a single block of MFCNT array. $C_F = 10wt\%$



FIGURE 9.3

(a) High resolution transmission electron microscope (HRTEM) images of iron-based nanoparticles intercalated inside CNT; (b) an iron-based NP showing the high crystallinity of the metallic nanoparticles. In that case the NP correspond to Fe₃C with 1: (100) and 2: (021) or (02-1) (2) planes observed along the [012] or [0-12] zone axis. Data refer to a sample synthesized with $C_F = 0.5$ wt%

We employed the X-ray photoemission and Raman spectroscopies to verify the crystalline quality of MFCNT arrays. Fig. 9.4 displays the carbon 1s (Fig. 9.4a) and iron 2p (Fig. 9.4b) core levels of the X-Ray photoemission recorded with a monochromatic source, a 150 mm hemispherical detector VSW and an overall resolution of 0.80 eV.

Wide scans (not shown) show carbon with small contributions of oxygen and iron. C1s core levels display one single graphitic carbon at 284.5 eV with a full width at half maximum (FWHM) of 1.1 eV. This confirmed the high quality of CNTs. The core level of Fe2p exhibits one contribution at 710.55 eV rather characteristic of oxide like Fe₂O₃ or hydroxide FeOOH and a minor another one at 707.8 eV in good agreement with what is expected from cementite Fe₃C or elemental α -Fe and γ -Fe. These contributions can hardly be separated with the resolution of the experiment [25]. We can in addition remark that the Fe2p intensities (Fig. 9.4b) is roughly proportional to the iron initial concentration *C*_F [24] and that the proportion of the minor contribution decreases with *C*_F (see insert of Fig. 9.4b). The presence of maghemite Fe₂O₃ nanoparticles inside the CNTs has been also detected in some samples by TEM observations, but only when the walls are damaged [24]. It is also speculated that a large amount of iron is deposited either on the surface of the substrate or on the walls of the CNTs and this iron is rapidly oxidized during air removal. Therefore this oxide contribution is more surface-sensitive, whereas carbidic iron, α -Fe and γ -Fe nanoparticles inserted into the CNTs are less-surface-sensitive and protected from further oxidation by carbon shell. It should be noted that these oxides are not ferromagnetic.

Fig. 9.5 shows the Raman spectra in the $1000 - 3000 \text{ cm}^{-1}$ range recorded with a Horiba spectrometer using an Ar laser at $\lambda = 532 \text{ nm}$ working in a backscattering geometry. Data refer to the samples synthesized with $C_{\rm F}$ in the range 0.5 – 10wt%.

Each spectrum is dominated by two bands, G (~ 1575 cm⁻¹) attributed to the twice degenerated deformation oscillations of the hexagonal ring in E_{2g} electronic configuration of D^4_{6h} crystal symmetry, and D (~ 1324 cm⁻¹) which corresponds to defective (edge, point defect, vacancy, etc.) hexagonal lattice of graphitic carbon. The G band is broadened in the case of CNT [26,27]. On the other hand, the presence of graphite particles of small size also gives rise to a D line in the Raman spectrum [28]. According to Pimenta at al. [29] and Cançado et al. [30], the in-plane size of graphite crystallite, L_a , can be determined from the following equation:



FIGURE 9.4

X-ray photoemission spectra of the MFCNT array synthesized with $C_F = 0.5$ wt% and $C_F = 10$ wt%. (a): C1s level and (b): Fe2p level. In the inset to Fig. 9.3b the spectrum with $C_F = 0.5$ wt% is magnified 10 times



FIGURE 9.5 Raman spectra of the MFCNT array at different $C_{\rm F}$ monitored in the 1000-3000 cm⁻¹ range

$$L_a = \frac{560}{E_{laser}^4} \frac{I_G}{I_D} \tag{1}$$

where E_{laser} is the laser excitation in eV, L_a is in nm. From our data ($E_{\text{laser}} = 2,33 \text{ eV}$) the average crystalline size of nanoparticle shell is estimated to be in the range 18 - 22 nm. Despite the fact that the Raman spectrum is the convolution of signals from nanotubes and nanoparticles shells, our estimation is in a good agreement with the electron microscopy findings.

Magnetic properties of samples were studied by measuring the zero filed cooled (ZFC) and field cooled (FC) magnetizations at H = 75 Oe as a function of temperature and isothermal magnetic hysteresis loops, M(H), at a given temperature. The ZFC-FC and M(H) dependences were measured using a SQUID magnetometer. The magnetic field was varied in the range -7 T to 7 T, within the temperature range 2 – 380 K. The magnetic moment was measured with the sensitivity of 10^{-8} emu. Magnetic field was always applied parallel to the CNT axis, i.e. perpendicular to the surface substrate. Taking into account the possible contribution of the diamagnetic response of the silicon substrate, we also measured the M(H) loops for the bare Si/SiO₂ substrate used in these experiments and we subtracted it from the signal of the samples. The $M_{sat}(T)$ dependencies in the temperature range 77 – 1400 K were also measured. For that we used the static ponderomotive method described in [31]. In this case the magnetic moment was measured with the precision of ± 0.01 emu/g. To avoid the oxidation during heating, samples were put in a vacuum ampoule under the pressure of 1.33×10^{-3} Pa.

For the elaboration of the magnetic data the exact mass of the ferromagnetic content was necessary to be known. For that we used the atomic absorption spectroscopy, which allowed obtaining the iron mass with a precision less than 0.01%.

Magnetostatic Parameters

To directly measure the Curie temperature, T_{C} , we performed the magnetization versus temperature measurements for all the studied samples. We use the ponderomotive static method for this purpose. A typical result of these measurements is displayed in Fig. 9.6 for samples A and C, respectively. The Curie temperature was evaluated by applying the Curie – Weiss law for the magnetization at $T \rightarrow T_{C}$, $M \sim (1-T/T_{C})^{1/2}$. In the inset to Fig. 9.6 we plot the M^{2} versus T dependence for the sample A, which gives us $T_{C} = 481$ K. This value corresponds well to the Curie temperature of Fe₃C known from literature (483K) [32,33].

At temperatures above the $T_{\rm c}$ value for cementite, however, the magnetization of samples still does not go to zero. This could be caused by the presence of other ferromagnetic phases, like α -Fe phase. Indeed, for the sample C measurements were performed up to T = 1060 K. In the temperature interval 850 K – 940 K the value of magnetization increases reflecting the growth of iron particles size due to their sintering. At temperatures above the Curie temperature of iron ($T_{\rm C}({\rm Fe}) = 1060 \, {\rm K}$) the magnetization becomes zero. On the other hand, the values of the saturation magnetization M_{sat} at room temperature were also estimated from these measurements. With the iron content determined by the atomic absorption, M_{sat} can be quoted to 194.1 emu/g for the sample A (C_F = 0.5%) and to 90.6 emu/g for the sample C (C_F = 10%). (This is to be compared with the saturation magnetization of α -Fe at room temperature (222 emu/g) and M_{sat} of Fe₃C at T = 300 K, which is known to be varied from 80 emu/g [34] to 125 emu/g [33].) This agrees well with the result of our previous study of the phase content of ferromagnetic phases in our samples by means of the Mössbauer spectroscopy. Indeed, for $C_{\rm F}$ = 10% the Fe₃C phase dominates while for small concentrations of ferrocene we get now a lower percentage of cementite Fe₃C and a higher content of α -Fe. Consequently, the percentage of α -Fe phase is lowered [15]. Therefore, the results of M(T) measurements in the high temperature range confirm the presence of two main ferromagnetic phases in our samples, cementite Fe₃C and α -Fe.



FIGURE 9.6

Temperature dependence of the magnetization M for the sample C (dots) and A (circles). Inset: M^2 versus temperature dependence for the sample A close to T_c . The arrows indicate the evaluated T_c values

The ZFC-FC curves reveal the typical features of an ensemble of ferromagnetic particles interacting with different strength with respect to their concentration [35]. In Fig. 9.7 the ZFC-FC magnetizations versus temperature for samples A (dashed lines) and C (solid lines) are shown. It is clearly seen that curves only coincide at the highest temperature measured. Therefore the blocking temperature T_B is set close above these values. Nevertheless, it is possible to extract useful qualitative information from the analysis of these data. In particular, a near flat FC curve for the sample C indicates strong interaction of nanoparticles, while the absence of such strength of the interparticle interaction for the sample A is evident. This is due to much lower concentration of nanoparticles in the last case [23].



FIGURE 9.7

ZFC and FC magnetizations versus T for samples A (dashed lines) and C (solid lines)

Since NPs in all studied samples are below both the Curie and blocking temperature, it is naturally to expect hysteresis and remanence properties. The isothermal magnetization curves, measured for the sample B at different temperatures are shown in Fig. 9.8. The ferromagnetic order presents up to the maximum temperature, at which measurements were performed, T = 380 K. The evolution of the symmetric magnetic hysteresis loops shows a narrowing tendency towards higher temperatures. Similar results were obtained for samples A and C.





Three main magnetostatic parameters can be extracted from the isothermal hysteresis magnetization curves, the saturation magnetization M_{sat} , the coercivity H_c and the remanent magnetization M_{rem} , as well as their dependences on the ferrocene content and temperature. Moreover, the performed M(H) measurements of samples synthesized with different C_F contents at different temperatures allowed studying both the temperature and ferrocene concentration dependence of the obtained parameters. In Fig. 9.9 we present the squareness (M_{rem}/M_{sat}) of the M(H) loops versus C_F at different temperatures, and in inset to Fig. 9.9 - the dependence of the coercivity H_c on C_F at T = 300 K is plotted.



FIGURE 9.9

Squareness versus the ferrocene content at different temperatures. Inset: Coercivity versus the ferrocene content at T = 300 K

Analysis of the result of Fig. 9.9 indicates that the squareness initially increases with C_F , and then it flattens out. For $C_F = 10\%$ the squareness at T = 300 K becomes less than for $C_F = 1\%$. For T = 2 K and 150 K the squareness between $C_F = 1\%$ and 10% practically does not change. For $C_F = 0.5\%$, however, it clearly drops. This indicates that NPs in the sample A are scattered and less interacting. This is in good agreement with the result of ZFC-FC magnetization, as reported in Fig. 9.7. The decrease of the squareness at high *T* values could be due to thermal fluctuations. The coercive field also increases with C_F . It is mostly due to the increase of the average size of the nanoparticles with ferrocene content. The obtained coercivities are larger than those reported for bulk Fe₃C [36]. At room temperature it

does not exceed the value of H_c = 100 Oe which is also of the order of H_c for cementite powder subjected to special treatment [37]. Here the H_c obtained is around 275 Oe at T = 300 K. This is the indication of the influence of the size effects on the H_c values, i.e. coercivities of single domain particles are generally much larger than those of bulk materials [35]. For this case and for intermediate temperatures H_c is expected to follow the law

$$H_{c}(T) = H_{c}(0) \left[1 - \left(\frac{T}{T_{B}}\right)^{\zeta} \right], \qquad (2)$$

where $T_{\rm B}$ is the blocking temperature of the largest particles in the system and the exponent ζ depends on the alignment of the particles [35]. For an assembly of aligned particles $\zeta = 0.5$ [38], while for randomly oriented particles $\zeta = 0.77$ [39]. In Fig. 9.10 we show the dependence of the coercivity $H_{\rm C}$ on $T^{0.77}$ values of the temperature for the highest (10%) and lowest (0.5%) $C_{\rm F}$. It follows from Fig. 9.10 that this dependence is clearly linear. Analysis of the experimental data with the exponent ζ = 0.5 gives a worse agreement.



FIGURE 9.10

Coercivity variations with temperature (2 K < 7 < 300 K) for two samples, A (open symbols) and C (closed symbols)

From the result of Fig. 9.10 we may evaluate the blocking temperature of the largest particles. The obtained $T_{\rm B}$ values are 385 K (sample C), 362 K (sample B) and 354 K (sample A). These data correspond well with what it could be expected for iron-based NPs. Indeed, the $T_{\rm B}$ values are less than the Curie temperature of cementite, reported in Fig. 9.6 as $T_{\rm C}({\rm Fe_3C}) = 481$ K, but higher than the range of ZFC-FC magnetization measurements. A gradual reduction of the blocking temperature with a decrease in the ferrocene content can be linked with a reduction in the average radius of ferromagnetic NP, $R_{\rm NP}$.

Random Anisotropy Model and Micromagnetic Parameters

On the basis of the obtained experimental data one can try to clarify the mechanism of magnetic interparticle coupling in our samples. In order to distinguish whether ferromagnetic nanoparticles are coupled via the exchange interaction, or their anisotropy energy is enough to compete the interparticle exchange coupling, we consider here the random anisotropy model (RAM) [3,40,41]. The RAM has been successfully applied in the past to explain the properties of amorphous [42] and nanocrystalline ferromagnets [43], as well as Fe₃C nanoparticles in CNTs [44]. Within the RAM it is possible to evaluate important micromagnetic parameters, such as the effective magnetic anisotropy K_{eff} , the anisotropy field H_a , the exchange field H_{ex} and the constant of the exchange coupling of the ferromagnetic material A. The key to the RAM is the assumption of the presence of chaos in the direction of the local magnetic blocks of size of ferromagnetic correlation length R_F [4]. The anisotropy field H_a and the exchange field H_{ex} and $H_{ex} = 2A/M_{sat}R_a^2$, respectively. Here R_a is the length over which the magnetic anisotropy axes are correlated. Usually in a nanocrystalline material R_a is assumed to be

equal to the radius of the nanoparticle, R_n [43]. Actually the value of R_F is expressed as $R_F \approx R_a (H_{ex}/H_a)^2$ [45]. The exchange coupling constant A could be calculated according to the relation $A = (k_B/8\pi)(M_{sat}/g\mu_B)^{1/3}(2.612/B)^{2/3}$ [46], where g is the Landé splitting factor, k_B is the Boltzmann constant, μ_B is the Bohr magneton and B is the Bloch's constant. The latter value was obtained from the analysis of the temperature dependence of the saturation magnetization [5] according to the Bloch's law, $M_{sat}(T) = M(0)(1-BT^{3/2})$, where M(0) is the saturation magnetization at T = 0 K. In Fig. 9.11 the temperature dependence of M_{sat} is shown for samples A and B.



FIGURE 9.11

Temperature dependences of the saturation magnetization (symbols) according to the Bloch's law. Solid lines represent the best linear fit to the experimental data. Data are for samples A (closed symbols) and B (open symbols)

The average radius R_n of the ferromagnetic nanoparticles in the assumption of a spherical form was calculated according to the standard relation $R_n = [(3/4\pi)25(k_BT_B/K_{eff})]^{1/3}$. The T_B values were obtained from the temperature dependencies of the coercivity, $H_c(T)$, see Fig. 9.10 and Eq. 2. The coercivity in the RAM is expressed as [41]

$$H_C \approx \frac{3.2R_n^6 K_{eff}^4}{A^3 M_{sat}}$$
(3)

Combining the formula for R_n and Eq. 3 we arrive to the expression for the effective anisotropy constant,

$$K_{eff}^{2} = \frac{H_{C}A^{3}M_{sat}}{114(k_{B}T_{B})^{2}}.$$
 (4)

Therefore, H_{ex} , H_a and K_{eff} values of the nanocomposite can be evaluated from such measurable quantities as H_C , M_{sat} , T_B and B. In particular, for the sample A we obtained the following set of micromagnetic parameters, $K_{eff} = 1.76 \times 10^4 \text{ J/m}^3$, $A = 5.18 \times 10^{-12} \text{ J/m}$, $H_{ex} = 5.73 \text{ kOe}$, $H_a = 2.73 \text{ kOe}$. For the sample B we got $K_{eff} = 1.25 \times 10^4 \text{ J/m}^3$, $A = 3.06 \times 10^{-12} \text{ J/m}$, $H_{ex} = 2.88 \text{ kOe}$, $H_a = 2.1 \text{ kOe}$. And for the sample C the parameters were $K_{eff} = 0.6 \times 10^4 \text{ J/m}^3$, $H_{ex} = 2.52 \text{ kOe}$, $A = 2.34 \times 10^{-12} \text{ J/m}$, $H_a = 2.0 \text{ kOe}$. All these data are for T = 50 K.

From these data it follows that the exchange constant, the magnetic anisotropy and the exchange fields, increase for smaller $C_{\rm F}$. The growth of the exchange constant A can be reasonably associated with the dominant role of the major ferromagnetic α -Fe phase at $C_{\rm F}$ = 0.5% [23]. At this concentration it does not exceed the value for bulk iron, $A_{\text{bulk,Fe}} = 2 \times 10^{-11} \text{ J/m}$ [47]. Increase of the magnetic anisotropy for small $C_{\rm F}$ values is related to less concentration of NPs distributed in CNT medium. This is in good agreement with the general expectations of RAM [3,4]. The $K_{\rm eff}$ values are less than for bulk Fe, $K_{\text{bulk, Fe}}$ =4.7×10⁴ J/m³ [48], while the anisotropy field, the coercivity field and the Bloch constant are much larger than for bulk Fe, $H_{a(bulk,Fe)} = 540$ Oe, $H_{c(bulk,Fe)} < 5$ Oe [48], and $B_{bulk,Fe} = 0.34 \times 10^{-5}$ K^{-3/2} [49]. The obtained high values of the anisotropy and coercivity fields could be the indication of the magnetization reversal of uncoupled or weakly exchange-coupled iron-based NP of small dimensions, $R_{\rm NP}$ < 18 nm. Moreover, with $C_{\rm F}$ increasing the dominant role of the Fe₃C phase starts to be important. The values of H_{a} , A, K_{eff} and B are slightly less than the corresponding values of bulk cementite $(A_{\text{bulk,Fe3C}} = 0.87 \times 10^{-11} \text{ J/m}$ [50], $B_{\text{bulk,Fe3C}} = 2.9 \times 10^{-5} \text{ K}^{-3/2}$ [51], $K_{\text{bulk,Fe3C}} = 4.2 \times 10^{5} \text{ J/m}^{3}$ [52], $H_{a,bulk,Fe3C}$ = 7 kOe). On the other hand, the coercivity field is essentially larger than for bulk Fe₃C. This is also naturally explained by the magnetization reversal of NP. The average NP dimension increases with $C_{\rm F}$. The increase of $H_{\rm C}$ with $C_{\rm F}$ is associated with the prevalent growth of the particle size, as well as with decrease of M_{sat} and A constant. The resulting change of these parameters dominates and the significant decrease of the effective anisotropy constant $K_{\rm eff}$ does not lead to the decrease of $H_{\rm cr}$ as it follows from the Eq. 3.

From the obtained parameters it follows that the dimensionless parameter $\lambda = H_a/H_{ex}$, which determines the strength of the magnetic anisotropy, is always less than 1. It means that weak anisotropy is a characteristic feature of all our samples.

Law of the approach to the saturation and correlation functions

To verify the physical meaning of the obtained micromagnetic parameters we analyzed the magnetization in the approach to saturation (H > 1 kOe). Analyzing the law of the approach to saturation (LAS) it is possible not only to check the micromagnetic parameters of the nanocomposite, but also to obtain useful information regarding the correlation in the orientation of the magnetic anisotropy axes of nanoparticles in real space [53]. Generally the LAS is expressed as [3]

$$\frac{\delta M}{M_{sat}} = \frac{M_{sat} - M(H)}{M_{sat}} \propto H^{\alpha}$$
(5)

where the exponent α depends on the relation between *H* and *H*_{ex}. For *H* << *H*_{ex} the exponent is α = -1/2, while for *H* >> *H*_{ex} it is α = -2 [45].

In Fig. 9.12 we plot the high field part of the magnetization loops, according to the Eq. 5, for sample A. In Fig. 9.13 we depict the same dependence for sample B. Data are for T = 50 K. It is seen the drastic change of the exponent α with small variations of C_F . Indeed, it was found that the experimental dependence for the sample synthesized with $C_F = 0.5\%$ is described by Eq. 5 only if the exponent is $\alpha = -2$ (Fig. 9.12). While for samples synthesized with $C_F = 1\%$ and 10% the exponent is $\alpha = -1/2$, which means $\delta M/M_{sat} \sim H^{-1/2}$. Moreover, the obtained LAS are valid for the sample with $C_F = 0.5\%$ in the field range 3 – 7 kOe, which covers the value of the exchange field for this sample $H_{ex} = 5.73$ kOe (the dashed vertical line in Fig. 9.12). For the sample B ($C_F = 1\%$) the LAS with the exponent $\alpha = -1/2$ is valid in the range 1 – 7 kOe, which also spans the value of H_{ex} = 2.88 kOe (the dashed vertical line in Fig. 9.13).



FIGURE 9.12

Analysis of the LAS for sample A ($C_F = 0.5\%$) according to the Eq. 5. Data are for T = 50 K. Solid line is for the best fit result. Vertical dashed line indicates the H_{ex} value. The range of the magnetic field in which the LAS according to the Eq. 5 is satisfied can be estimated from the upper horizontal axis of the figure

In the case when the experimental range of H crosses the H_{ex} value, analysis of the LAS should be done within the more general expression [4,45,54]

$$\frac{M(H)}{M_{sat}} = 1 - \frac{\lambda^2}{30p(H)} \int_0^\infty d^3 r \exp[-p(H)r] r^2 C(r)$$
(6)

with $p^2 = H/H_{ex}$, $r = x/R_a$, $\lambda = (2/15)^{1/2} (K_{eff}/A)R_a^2$ and x as a coordinate. C(r) is a correlation function describing the distance over which the magnetic anisotropy axes are correlated, scaled with C(r = 0) = 1 and C(r >> 1) = 0 [43,54]. Correlation function is determined using the inverse Laplace transform of the Eq. 6.



Analysis of the LAS for sample B ($C_F = 1\%$) according to the Eq. 5. Data are for T = 50 K. Solid line is for the best fit result. Vertical dashed line indicates the H_{ex} value. The range of the magnetic field in which the LAS according to the Eq. 5 is satisfied can be estimated from the upper horizontal axis of the figure

The analysis performed according to the Eq. 6 revealed that the correlation function for the sample A is Fermi-Dirac-like function

$$C(r) = \frac{1}{1 + \exp\left(\frac{r - r_{1/2}}{2}\right)},$$
(7)

where $r_{1/2}$ is a coordinate at which the value of the correlation function is equal to 1/2. This correlation function is shown in Fig. 9.14 by the solid line. The correlation of the magnetic anisotropy axes is present on macroscopically large distance, up to hundreds of nanometers. Correlation functions for sample B and C differ significantly from that for the sample A. The analysis performed on the base of Eq. 6 revealed that the correlation function for these samples is Bessel function of the first kind

$$C(r) = \beta^{-1/2} r^{\frac{\nu-4}{2}} J_{\nu} \left(2\beta^{1/2} r^{1/2} \right), \tag{8}$$

where β and ν are constants. This function decays rapidly on distance of a few nanometers, which means the rapid decrease of the magnetic anisotropy contribution and increase of the exchange interaction between nanoparticles. As an example, in Fig. 9.14 we show the correlation function for the sample B (dashed line). The same type of the correlation function was also obtained for the sample C (not shown here).



Correlation functions for samples A (solid line) and B (dashed line) and the correlation function for the powder obtained from the sample A (dotted line)

Coherent anisotropy and CNT alignment

According to our opinion, the obtained Fermi-Dirac-like correlation function for the sample A is determined by the influence of the CNT alignment. Indeed, all the results presented up till now in this chapter are related to aligned samples (see Fig. 9.1). The obtained extended order for the sample A ($C_F = 0.5\%$) means the absence of the dominant role of the random anisotropy in it. On the other hand, the observed LAS of the type $\delta M/M_{sat} \sim H^2$ usually is associated with the magnetization of uncoupled single domain nanoparticles, for which the exchange interaction is negligibly small [45]. Therefore, it is reasonable to assume that for sample synthesized with low ferrocene concentration, for which all the ferromagnetic nanoparticles are localized inside the inner channels of CNTs [23], the CNT alignment could reinforce the coherent (i.e. non random) magnetic anisotropy, which usually is much weaker than the random one [3]. In other words, the CNT alignment together with the ferromagnetic nanoparticles localization in the inner CNT channels facilitates the appearance of the orientational order in the sample.

The importance of the CNT alignment on the extended orientational order was proved directly by studying the LAS for a powder formed from the aligned sample synthesized with $C_{\rm F}$ = 0.5%. For powder the alignment is destroyed and sample consists of randomly oriented blocks. Inside each block CNTs are aligned, but the entire sample consists of misaligned nanotubes (see Fig. 9.2). The high field part of the magnetization curve plotted according to the Eq. 5 for the powder formed from the aligned sample with $C_{\rm F}$ = 0.5% is shown in Fig. 9.15. It is clearly seen that the experimental data are described according to the Eq. 5, but with the exponent α = -1/2 instead of α = -2, as it was for the aligned sample A (see Fig. 9.12).

As a consequence of such exponent, the correlation function for the powder which describes the experimental data was as for samples B and C, see dotted line in Fig. 9.14.



Analysis of the LAS for powder sample synthesized with $C_F = 0.5\%$ according to the Eq. 5. Data are for T = 50 K. Solid line is for the best fit result. Vertical dashed line indicates the H_{ex} value. The range of the magnetic field in which the LAS according to the Eq. 5 is satisfied can be estimated from the upper horizontal axis of the figure

The weak oscillating character of the obtained correlation functions for samples B, C and powder formed from sample A does not mean the oscillation of the magnetic anisotropy. According to our opinion, it could be mostly caused by the peculiarities in the exchange interparticle interaction and influence of the CNT matrix on it. Indeed, the indirect exchange coupling characterizes the carbon nanotubes [6]. This could cause the oscillating character of the exchange coupling, which reflects in the weakening and strengthening of the magnetic anisotropy contribution along the CNT. But this mechanism is absent in the RAM which has been applied for the discussion of the experimental data.

Conclusions

The relation between the exchange interaction and magnetic anisotropy for different concentration of iron based nanoparticles in aligned carbon nanotube arrays has been studied. Samples have been obtained *in situ* during the floating catalyst CVD. The analysis of the experimental data showed that the LAS is proportional to the ratio $(H/H_{ex})^{-2}$ for sample synthesized with lowest ferrocene concentration $C_F = 0.5$ wt%. When $C_F \ge 1$ wt% the obtained LAS is proportional to $(H/H_{ex})^{-1/2}$. Moreover, the obtained values of the exchange field are always in the range where the observed laws of the approach to saturation are valid. This fact entails finding the correlation functions that determine the contribution of the random anisotropy. It is shown that, for $C_F = 0.5$ wt% the correlation function. In this case the exchange interaction between magnetic nanoparticles is weak and the main contribution to the energy makes the random and coherent anisotropy. This effect is caused by the fact that the CNT alignment together with the ferromagnetic nanoparticles localization in the inner CNT channels facilitates the appearance of the orientational order in the sample.

For aligned samples synthesized with $C_F \ge 1$ wt% as well as for disaligned samples with $C_F = 0.5$ wt% the correlation function decays rapidly, is oscillatory and is described by the Bessel function of the first kind. In this case the main mechanism of the interparticle interaction becomes the exchange coupling. It could be caused by the indirect exchange coupling which is characteristic of carbon nanotubes and

reflects the competition between the exchange and anisotropy interactions of iron based nanoparticles in CNT arrays.

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