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Magnetic and structural properties of Co nanoparticles in a polymeric matrix

S.P. Gubin^a, Yu.I. Spichkin^a, Yu.A. Koksharov^b, G.Yu. Yurkov^a, A.V. Kozinkin^c,
T.I. Nedoseikina^c, M.S. Korobov^{a,*}, A.M. Tishin^b

^a*N.S. Kurnakov Institute of General and Inorganic Chemistry RAN, Moscow 117091, Russia*

^b*Physics Faculty, M.V. Lomonosov Moscow State University, Moscow 119899, Russia*

^c*Research Institute of Physics, Rostov State University, pr. Stachki 194, Rostov-on-Don 344104, Russia*

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Abstract

Magnetic, magnetic resonance and structural properties of Co nanoparticles in polyethylene matrix have been investigated. The materials were prepared by a method of thermal decomposition of cobalt formate in the polyethylene melt in a mineral oil and contained 4 wt% of Co. Transmission electron microscopy data showed that the particles diameter was 4 nm. According to EXAFS studies the particles can be presented as consisting of metallic core and a surface shell interacting with the surrounding matrix. Magnetic and magnetic resonance studies showed that the material has high blocking temperature (about 600 K) and the magnetic anisotropy constant of the nanoparticles is of an order of magnitude higher than that in a bulk cobalt. The origin of the high magnetic anisotropy of the Co nanoparticles is related to the surface effects. The material has relatively high hysteresis at room temperature (590 Oe), which makes it promising for magnetic recording applications.

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1. Introduction

Materials containing magnetic particles of nanometer sizes have been attracting the special attention of investigators in recent years. The

unique properties of nanoparticles are determined first of all by the fact that a large number of atoms (10%) in a nanoparticle belongs to its surface. The violation of crystal symmetry, coordination number, ligands type, etc. on the surface subject the surface atoms to conditions radically different from that in the bulk of the material. Besides, the surface atoms interact with the material of matrix where they are contained. From this point of view a matrix should have an essential influence on the properties of the particles. Investigation of the

*Corresponding author. Laboratory of polynuclear and Cluster compounds, N.S. Kurnakov Institute of General and Inorganic Chemistry, Leninskii pr. 31, Moscow 119991, Russia. Tel.: +7-095-9547136; fax: +7-095-9541279.

E-mail address: korobovigic@yandex.ru (M.S. Korobov).

properties of such materials has both fundamental and practical interest. Polymeric matrices with embedded magnetic nanoparticles constitute an important class of nanostructures. These materials are especially important for practical applications, since the polymeric technology allows fabricating components of various forms and mechanical properties.

Cobalt, which is a ferromagnetic metal with the currently highest Curie temperature (1390 K), is widely used in industry today. Co is interesting in the form of nanoparticles, in particular, for the creation of materials for high-density digital magnetic recording. As a rule, a magnetic recording material represents a nonmagnetic medium (matrix) with more or less uniformly distributed magnetic particles or films with granulated structure. Magnetic particles (granules) should have coercive force high enough to prevent from demagnetization (e.g. by thermal agitations). Besides an interaction between the particles should be weak, so that magnetization reversal of one of the particles (or a group of particles forming “a bit of information”) will have small influence on the neighboring particles. It should be noted that in modern magnetic materials Co is usually used in combination with other materials, e.g., as CoPtCr-Ta alloy for computer hard disks. It is believed that Pt stabilizes Co hexagonal structure, which has better magnetic properties than cubic modification and combination Cr-Ta weakens interactions between the granules [1]. The average size of the magnetic granules in the modern materials for magnetic recording is about tens of nanometers. Smaller nanoparticles could have a different ratio of elements, which is optimal for magnetic recording purposes. The investigation of magnetic nanoparticles of a typical size below 10 nm, which contain only cobalt, is vital before studying of more complex compositions.

Magnetic properties of Co nanoparticles have been investigated in a number of works [2–18]. It was found that the properties of the particles strongly depend on methods and conditions of preparation. However, there are some common regularities, which are as follows: (i) FCC crystal structure is frequently observed in Co nanoparticles and (ii) their magnetic anisotropy is usually

enhanced in comparison with the bulk state, which is due to surface effects. For most manufacturing techniques Co nanoparticles are superparamagnetic at room temperature. An example of the exclusion is the work [19], where Co nanoparticles with a typical diameter of 5 nm, obtained on the graphite surface, had the average blocking temperature of 320 K.

However, it should be noted that the question about the cobalt structure type realizing in nanomaterials is now under discussion. As it was shown in some papers [20–23], the FCC-type structure is formed in Co nanomaterials. Another authors [24–28] reported that many cobalt nanoparticles display mixed structures with HCP and FCC character. It is very important to note that nearly all studied Co nanomaterials are films, which have metals with FCC-structure substrate. As it was shown in Refs. [25–27] below three monolayers the cobalt is prolonging the FCC lattice of substrate but beyond this thickness, HCP domains appear. The mixed structure was revealed in Co “lines” carbon nanocapsules [29]. The cobalt has FCC structure in Co-filled carbon nanocapsules that can be due to “small particle nature of the material and/or “quenching” effects” [30].

In this work, we have undertaken investigations of structural, magnetic resonance and magnetic properties of a material containing Co nanoparticles embedded in a polyethylene matrix and prepared by thermal decomposition (thermolysis) of a metal containing precursor (MCP) in the polymer melt. The obtained nanoparticles have the mean diameter of ~ 4 nm and are characterized by rather high blocking temperature (about 600 K). The material also has a relatively high coercive force (nearly 600 Oe), which allows it to be regarded as a promising material for magnetic recording.

2. Samples preparation

The material containing Co nanoparticles in polyethylene matrix was prepared by the method of thermal decomposition (thermolysis) of the cobalt formate in the polyethylene melt in a mineral oil as described in the work of Ref. [31].

Synthesis was performed in argon flow at 290–300°C. The velocity of argon flow provided rapid removal of ligands and solvent from the reactor vessel. Necessary amount of cobalt formate was introduced in the reaction mixture under intensive mixing. After cooling down to room temperature the obtained product was extracted from the reaction vessel and washed out from the oil by benzene. Then the product was dried in vacuum and was stored in air for further investigations. The obtained composite was the powder with dark gray color. Elemental analysis showed that cobalt content in the material is ~ 4 wt% (C, 82.20%; H, 13.43%; Co, 4.03%; $\Sigma = 99.66\%$). Taking into account the accuracy of each elements content determination, the content of oxygen in the sample cannot exceed 0.1 wt% (or no more than 1 atom oxygen on 10 Co atoms).

3. Transmission electron microscopy

In order to confirm the presence of nanoparticles in the material and to determine their dimensions we have used transmission electron microscopy (TEM). The investigations were carried out on the JEM-100B (JEOL) electron microscope working at 100 kV. The powder-like sample was dispersed by ultrasound in ethyl alcohol. Then the suspension was placed on a carbon grid and dried. The final ultrafine polymeric powder was used to make TEM micrographs.

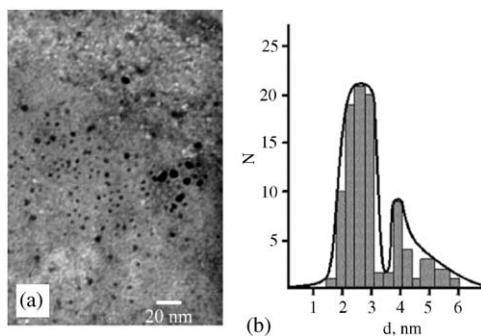


Fig. 1. TEM photography (a) and histogram (b) of the particles dimensions distribution for the sample containing 4 wt% Co in polyethylene matrix.

Fig. 1 shows TEM micrograph of the sample and histogram of the particle sizes distribution constructed on the base of the micrograph. As one can see, there are dark inclusions on the light background (polymeric matrix) corresponding to the nanoparticles. According to the TEM data the mean diameter of the particles in the sample is 4 nm and their shape is nearly spherical.

4. EXAFS studies

The Co K-edge EXAFS of Co nanoparticles stabilized in polymer matrix was measured in transmission mode using laboratory EXAFS spectrometer designed on the basis of an X-ray spectrometer DRON-3 M [32]. Quartz (1340) was used as a crystal-analyzer. UWXAFS software [33] was utilized for the background removal, EXAFS extraction and normalization of the absorption edge. Fourier transform of the EXAFS function was carried out over k -range from 2.5 to 12.0 \AA^{-1} .

The structure of metal Co is HCP at room temperature and FCC at 477 K [34]. Each of these structures or their combination can be realized in Co nanoparticles. As one can see from the comparison of the modulus of the Fourier transform (MFT) of the Co K-edge EXAFS for the Co sample and calculated one for metal HCP and FCC Co structures (Fig. 2), MFT of HCP Co differs from MFT FCC Co insufficiently. It is impossible to define what structure type of Co realizes in nanoparticles. As it was shown in Section 1, the question about Co structure in nanosize state is not clear at present. On the basis of the analysis of literature data and the value of temperature of our sample synthesis we suggested that HCP-structure is more stable than FCC at room temperature. Moreover we used as HCP, as FCC structures of Co nanoparticles in the simulation. As the analysis of MFT cannot give exact information about the type of the structure, the final choice of structure was made on the basis of simulation results (from comparison between calculation EXAFS function and experimental one). So, the analysis of Co sample EXAFS spectrum was carried out using HCP Co structure.

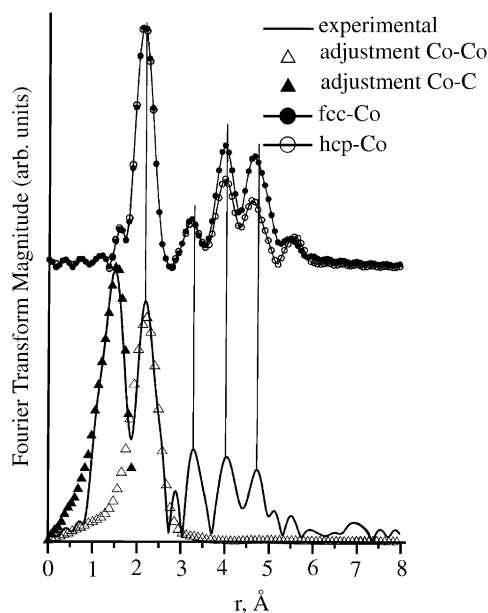


Fig. 2. Fourier transform modules of the EXAFS functions of the investigated sample and calculated EXAFS functions of metallic HCP and FCC cobalt.

The EXAFS MFT (Fig. 2) provides information about the nearest neighbor environment of Co atoms in nanoparticles. The MFT of the normalized EXAFS curve passes through maxima at $r_j = R_j - \alpha_j$, where R_j is the distance from the absorbing atom to the atoms of the j th coordination sphere, and α_j is the phase correction which can be determined from the EXAFS spectra of compounds with known structures or by calculation.

Fig. 2 shows that MFT of Co nanoparticles has all features proper for Co metal except the first peak at $r = 1.52 \text{ \AA}$. This peak can correspond to Co–O or Co–C coordination shell. According to elemental analysis the sample contains less than 0.1% wt. of oxygen. Investigation of Co $K\beta_5$ -spectrum also indicates that the Co–O interactions are absent. So, the first peak is a result of Co–C interactions. However, the features typical for Co carbides are absent on the MFT. This means that cobalt carbides do not form in the particles volume and only surface Co atoms interact with carbon atoms. Comparability of amplitudes of Co–C ($r = 1.52 \text{ \AA}$) and the first Co–Co ($r = 2.18 \text{ \AA}$) peaks indicates large amount of Co–C bonds. It

is possible if the number of surface nanoparticle atoms is comparable with the number of atoms in the bulk of a nanoparticle that agrees with average size of the nanoparticles measured by TEM.

The fitting was carried out in r -space over the range 1.8–2.8 \AA . According to this data the Co–Co interatomic distance R is equal to $2.561 \pm 0.015 \text{ \AA}$, coordination number (N) is 4 and mean square deviation of the interatomic distance from its equilibrium value (σ^2) is equal to $0.012 \pm 0.005 \text{ \AA}^2$. Such set of parameters corresponds to minimum deviation of calculated EXAFS MFT function from experimental one (3%). As one can see, the Co–Co interatomic distance is close to its value in metal Co, where $R = 2.50 \text{ \AA}$. Decreasing the coordination number from 12 in metal to 4 in nanoparticles can result from large amount of surface atoms and also can be due to formation of imperfect crystallographic structure, namely a lattice with the vacancies. Assumption about the imperfect structure agrees well with the obtained Co–Co interatomic distance, which is larger than that in the Co metal by $0.05 \pm 0.01 \text{ \AA}$. In fact, if the formed structure has vacancies than it is less dense that can lead to increasing of the average interatomic distance. In addition, in this case the amplitude of metallic peak decreases and as a result the carbon peak is more prominent.

For surface Co atoms interacting with carbon atoms it is difficult to obtain the structural parameters by the fitting procedure. A set of different values of the structural parameters, especially N and σ^2 was obtained by the fitting for the same deviation of the theoretical EXAFS MFT function from the experimental one (R -factor). The best fitting was achieved for Co–C intraatomic distance $R = 2.07 \text{ \AA}$, coordination number from 4 to 6 and σ^2 from 0.003 to 0.01 \AA^2 . Such a set of parameters correspond with the R -factor value of 3%. The obtained Co–C interatomic distance is in good agreement with that in metalorganic compounds of cobalt. The coordination number is also typical for metalorganic compounds.

Therefore, the following model of Co nanoparticles stabilized in polyethylene matrix can be suggested. Nanoparticles consist of a metallic core and a surface layer. Metallic core has Co structure

with vacancies, e.g. rarefied (friable) structure. The surface of the Co nanoparticles interacts with carbon atoms like in metalorganic compounds of cobalt. This surface layer protects the particle from penetration of other carbon or oxygen atoms from air—as a result the crystal structure of metallic Co preserves in the volume of the particle. EXAFS investigations made after 3 and 6 months of the sample preparation confirmed that the crystal structure of Co nanoparticles is stable and does not change with time.

5. Magnetic and magnetic resonance properties

We have measured temperature and field dependencies of magnetization with the help of the vibrating sample magnetometer (model PARC-155, Princeton Applied Research) with a flow helium cryostat and a home-made high temperature insert. The magnetometer sensitivity is better than 5×10^{-5} emu. The magnetic measurements were carried out in the temperature range from 4.2 to 380 K and in magnetic fields up to 4.5 kOe. Measurements of hysteresis loops were made by the first saturating of the sample in the field of 4.5 kOe. EPR studies were carried out using X-band (~ 9.2 GHz) spectrometer Varian E-4. The temperature was controlled by the nitrogen temperature system E-257 (Varian) from 295 to 495 K and platinum thermoresistor with an accuracy of ± 1 K. The width of resonance spectra lines was determined by “peak-to-peak” method. The registration and the analysis of a microwave absorption field hysteresis in low magnetic fields were conducted according to a procedure described in Ref. [35].

Fig. 3 presents the hysteresis loops of the sample containing 4 wt% of Co in polyethylene matrix measured at 4.2, 77 and 295 K. Rather high coercive force (590 Oe) observed even at room temperature witnesses the system of nanosize magnetic particles in the sample in the blocked state. The coercive force increases under cooling reaching the value of 680 Oe at 4.2 K. The magnetization value in the maximal used magnetic field ($H_{\max} \approx 4.5$ kOe) also increases under cooling. Simultaneously the magnetization field behavior

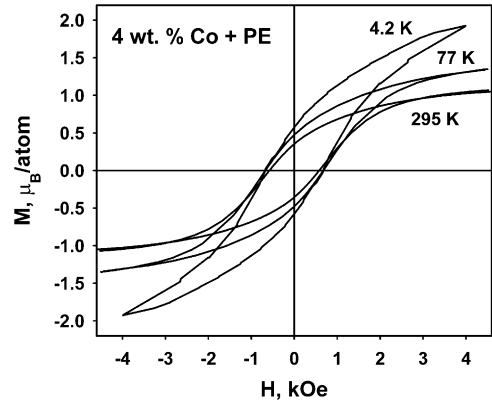


Fig. 3. Hysteresis loops of the investigated sample at 4.2, 77 and 295 K.

changes qualitatively: the room temperature magnetization at H_{\max} approached saturation value, while at 4.2 K any saturation is absent and only the minor hysteresis loop is observed. Such behavior can be related with the magnetic anisotropy rising in the low temperature region. The high magnetization value— $1.05 \mu_B/\text{atom}$ at 295 K and $1.95 \mu_B/\text{atom}$ at 4.5 K in the field of 4.5 kOe attracts attention. According to Ref. [36] the saturation magnetization in bulk Co is $1.7 \mu_B/\text{atom}$, i.e. in our samples we have higher saturation magnetization values per Co atom than in a bulk state.

According to the Stoner–Wohlfarth model the coercive force temperature dependence for a system of superparamagnetic particles in the blocked state can be described by the following equation [37,38]:

$$H_c(T) = H_c(0)(1 - aT^\beta), \quad (1)$$

where $H_c(0)$ is the coercive force value at $T = 0$ K, a is a coefficient and exponent $\beta = \frac{1}{2}$. However, in the investigated sample with 4 wt% of Co in polyethylene matrix the dependence (1) with $\beta = \frac{1}{2}$ did not obey the experimental data. The best fit was achieved for $\beta = 2$. Fig. 4 shows experimental points and the simulation curve $H_c(T)$ with $\beta = 2$ for the temperature dependence of the coercive force in the sample under investigation. The extrapolation to the high temperature region shows that the coercive force should become equal to zero at 560 K. This temperature can be regarded as a blocking temperature T_b of the sample.

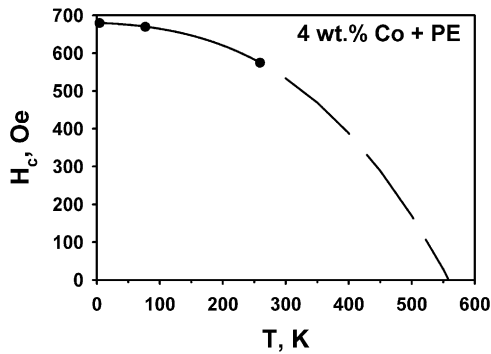


Fig. 4. Temperature dependence of the coercive force of the investigated sample.

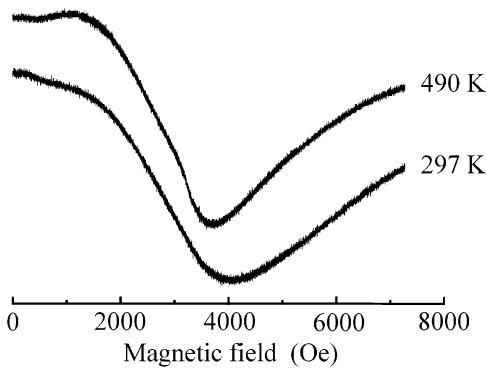


Fig. 5. Typical EPR spectra of Co nanoparticles at room temperature and at the maximal temperature, which was achieved in the experiments.

Typical magnetic resonance spectra of the Co nanoparticles system are shown in Fig. 5. First of all it should be noted that the resonance lines have rather large width. For the maximum temperature of our experiments (~ 500 K) the linewidth ΔH_{pp} was about 2500 Oe. Cooling down to room temperature leads to ΔH_{pp} increase up to 3000 Oe. At all temperatures the resonance line is significantly shifted from the field, corresponding to the free spin spectroscopic factor $g = 2$, to the low fields (Fig. 5). At high temperatures it is possible to discern the second narrower and weaker line near $g = 2$.

The second feature of the investigated magnetic resonance spectra is a pronounced hysteresis of the microwave absorption signal in low fields. Temperature dependence of a phenomenological parameter ΔZ_{eff} (in per-unit), which is proportional

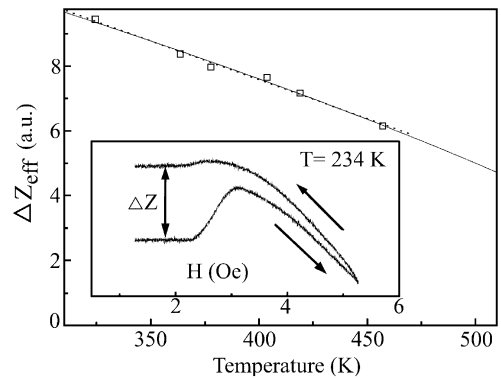


Fig. 6. The temperature dependence of the low-field microwave absorption. Insert shows how the parameter ΔZ_{eff} has been measured. The arrows indicate the increasing or decreasing of the external magnetic field during the recording procedure. Solid line shows the best simulation of the $\Delta Z_{eff}(T)$ by the function $(T_0 - T)^\alpha$, where $T_0 = (630 \pm 140)$ K; $\alpha = 0.7 \pm 0.4$. Dashed line shows the best simulation of the $\Delta Z_{eff}(T)$ by the function $A + BT$, where $A = 17.0 \pm 0.5$; $B = (-0.024 \pm 0.001) \text{ K}^{-1}$.

to a remanent magnetization [35], is presented in Fig. 6. The dependence $\Delta Z_{eff}(T)$ can be with enough accuracy approximated by a linear dependence $A + BT$, where $A = 17.0 \pm 0.5$ and $B = (-0.024 \pm 0.001) \text{ K}^{-1}$. The parameter ΔZ_{eff} becomes zero at $T = -A/B \approx 700$ K. Because many magnetic characteristics (e.g., the saturation magnetization, the susceptibility) obey an exponential law on approaching the temperature of the phase transition from the magnetically ordered to the disordered state, we fitted experimental $\Delta Z_{eff}(T)$ dependence by the exponential function $(T_0 - T)^\alpha$ (see Fig. 6). The fitting parameters were found to be $T_0 = (630 \pm 140)$ K and $\alpha = 0.7 \pm 0.4$. So, according to the magnetic resonance data, the remanent magnetization becomes zero at the temperature about 600 K, in good accordance with the magnetization data.

The investigated samples were also subjected to a heat treatment in air under a temperature of 280°C for 2 h. The results of magnetic measurements at the room temperature on the as-prepared and heat-treated samples are presented in Table 1. As one can see the heat treatment does not lead to the change of the coercive force value, but to about twice increase of the sample magnetization. This magnetization change can be connected with the

Table 1

Coercive force H_c , remanent magnetization M_r , magnetization in the field of 4.5 kOe at room temperature for the as-prepared and heat-treated at 280°C for 2 h samples, containing 4 wt% of Co in polyethylene matrix

	H_c (Oe)	M_r (μ_B)	$M_{H=4.5}$ (μ_B)
As-prepared	590	0.35	1.05
Heat-treated	590	0.62	1.96

crystal structure transformation of the particles during heat treatment.

6. Discussion

One of the interesting results obtained in this work is that the magnetization values per Co atom in the investigated nanoparticles is higher than the saturation magnetization in a bulk state. Theoretical calculations [11–15] predict enhanced magnetic moment in nanoparticles of 3d transition metals Fe, Co and Ni compared to the bulk value. This enhancement was related with 3d band narrowing in the surface layer of the particle due to a reduced coordination number of 3d atoms at the surface. This effect is especially pronounced in small particles where the relative number of atoms on the surface is high and they play an essential role in the forming of the particle magnetic properties. The magnetic moment enhancement was observed experimentally in Co particles with diameter 1–2.5 nm in a polymeric matrix [5], in 1.8–4 nm Co particles in micelles [22], and in experiments with Fe, Co and Ni superparamagnetic clusters in molecular beams [15–18]. In the works [17,18] it was established that Co magnetic moment in the cluster is 2.2 μ_B /atom.

It is known that in cobalt oxides CoO and Co₃O₄ the magnetic moments per Co ion of 3.52 and 3.25 μ_B , respectively, are observed [39]. Since both oxides are antiferromagnets, the significant external magnetic field is required to give noticeable contribution to the particle magnetic moment. This is hardly possible in the fields used in our studies. That is why it is reasonable to assume that the observed Co magnetic moment enhancement has the same origin, which was discussed in Refs.

[11–15]. It should also be noted that according to the elemental analysis the oxygen content in our samples cannot exceed 0.1 wt%. Additional Co magnetic moment enhancement can come from imperfection of the nanoparticles crystal structure (vacancies) discussed in the section “EXAFS studies”. This factor can also change 3d band structure towards more localization of 3d electrons and increasing of the atom magnetic moment.

Another important result is the high blocking temperature observed in the investigated sample (about 600 K). On the basis of the blocking temperature value the magnetic anisotropy constant of Co nanoparticles can be estimated using the following equation [38]:

$$T_b = KV/25k_B, \quad (2)$$

where K is the anisotropy constant, V the volume of the particle, and k_B the Boltzmann constant. Using the data about the particle mean diameter (4 nm from TEM) we can obtain from Eq. (2) $K \approx 6 \times 10^7$ erg/cm³, which is more than order of magnitude higher than the magnetic anisotropy constant in bulk Co ($\sim 4 \times 10^6$ erg/cm³ [36]).

The maximal value of the energy of the shape anisotropy is determined by the formula for the long circular cylinder [36]:

$$E_s = \pi I_s^2, \quad (3)$$

where I_s is the saturation magnetization. For Co this energy is about 2.3×10^6 erg/cm³ (assuming for Co $I_s \approx 1500$ Gs at 20°C [36]), which is at least one order of magnitude less than the anisotropy constant in the investigated material. Besides, according to our TEM data, the particles have mainly spherical form. Suggesting that the main contributions in the particle anisotropy are the contributions from the volume anisotropy and from the surface anisotropy, one can present the anisotropy constant of the particle as [40]

$$K = K_V + \frac{6}{d} K_s, \quad (4)$$

where K_V and K_s are the volume and surface contributions in the particle anisotropy, respectively. According to the data of the work [40], the values of K_V in iron nanoparticles and in the bulk material are of the same order of magnitude.

Assuming that this is true also for cobalt, we can estimate the surface anisotropy constant K_s in the investigated nanoparticles. It is equal to ~ 3.7 erg/cm². According to the work [41], where the exchange unidirectional anisotropy in the layered structures with cobalt oxides was considered, the surface anisotropy constant takes the values in the interval from 0.01 to 3.5 erg/cm² at the temperatures below 150 K. Taking into account high blocking temperature in the investigated samples, as well as relatively low values of Neel temperatures for CoO and Co₃O₄ (291 and 40 K, correspondingly [39]), we can conclude that the exchange unidirectional anisotropy is not the main reason of the enhanced high-temperature magnetic anisotropy in the investigated Co nanoparticles.

The surface anisotropy of the metallic particles can also be related to the change of 3d electrons band structure on the surface as a result of the electric crystalline potential changing and, as a consequence, changing of the spin–orbit coupling, which forms anisotropic properties of a metal [42]. Theoretical estimations in the framework of the band theory give for 3d electrons the values of surface anisotropy in the range from 0.1 to several erg/cm² [42–44]. In accordance with the Neel model [45], which considers the dipole–dipole interactions between magnetic moments on the surface, the value of the surface anisotropy should be of the order of 1 erg/cm². So, the value of the surface anisotropy constant for Co nanoparticles in our samples could be explained by the disturbance of crystal structure regularity on the surface.

Jamet et al. [9] and Hickey et al. [10] studied the magnetic properties of Co nanoparticles embedded in Cu and Nb metal matrices. For Co in Cu the anisotropy constant was equal to 3×10^8 erg/cm³. For Co in Nb the cobalt nanoparticles with the mean diameter of 3 nm demonstrated low blocking temperature ($T_b = 40$ K) and the anisotropy constant about 2.2×10^5 erg/cm³. The magnetic behavior of Co nanoparticles with the diameter of 20 Å and the concentration of 12 vol% in the polymerized propane film was studied by Laurent et al. [46]. The blocked state was not found down to 6 K, which implies the value of the anisotropy constant as in the bulk material. The observed significant K value scattering can be related partly to the matrix

properties, namely to differences in interactions between particles and the matrix.

The magnetic resonance spectra of the studied Co nanoparticles obey general regularities typical of ferromagnetic nanoparticles: the resonance line narrows with temperature increasing and at high temperatures the second narrow line becomes noticeable in the spectrum. The unusual feature of the studied Co nanoparticles (e.g., in comparison with Fe nanoparticles) is the essential width of the resonance line (above 2 kOe for all temperatures). To estimate the anisotropy energy from the magnetic resonance data we used the results of de Biasi et al. [47]. For single-domain randomly oriented spherical nanoparticles the width of a magnetic resonance line cannot be smaller than the anisotropy field H_a with correction to superparamagnetic fluctuations. The anisotropic field for FCC Co $H_a = K/I_s \approx 1600$ Oe. After taking into account the thermal fluctuations (for the particles with the diameter of 4 nm) this value decreases down to about 400 Oe. Because in our case the resonance linewidth at 295 K is ~ 3000 Oe, the anisotropy field (and, correspondingly, the anisotropy energy) is about 7–8 times larger than in the bulk cobalt. This does not contradict the data obtained from the magnetization measurements.

7. Conclusions

The investigations of the static magnetization and the microwave resonance absorption have showed that Co nanoparticles in a polyethylene matrix display a set of interesting properties. First of all it is enhanced (in comparison with the bulk value) magnetic moment per atom. Secondly, it is the record blocking temperature, notably higher than the room temperature. The high blocking temperature points to the high magnetic anisotropy, which can be apparently related to surface effects. The material also has a relatively high coercive force at room temperature, which makes it promising for magnetic recording applications. However, it is desirable to increase this parameter, which can be achieved by the preparation of Co-based nanoparticles with the more complex

composition, e.g. Co-Pt nanoparticles. Now this work is in progress.

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