Electroless Synthesis of Cobalt Nanowires in Magnetic Field and their Characterization by Resonant Magnetometry Methods

Tatiana Gegechkori
Department of Condensed Matter Physics, Andronikashvili Institute of Physics, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
tatagegechkori@yahoo.com (corresponding author)

Grigor Mamniashvili
Department of Condensed Matter Physics, Andronikashvili Institute of Physics, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
mgrigor@rocketmail.com

Tinatin Zedginidze
Department of Condensed Matter Physics, Andronikashvili Institute of Physics, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
tinikozedginidze@yahoo.com

Tamar Petriashvili
Department of Condensed Matter Physics, Andronikashvili Institute of Physics, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
tamuna777petriashvili@yahoo.com

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ABSTRACT

In this paper, a simple and effective low-temperature electroless chemical method that provides the synthesis of cobalt micro- and nanowires due to the processes of self-organization of magnetic cobalt nanoparticles under the influence of a magnetic field, using the technology of chemical synthesis of magnetic nanoparticles and nanowires is proposed. Cobalt nanoparticles have magnetic dipole moments. An external magnetic field forces them to be oriented parallel to it. Dipole-dipole interactions between magnetic nanoparticles lead to attraction between cobalt nanoparticles leading to their self-organization into nanowires, reducing their total energy. The resulting smaller nanoparticles fill the gaps between the ordered nanoparticles, leading to the formation of smooth cobalt nanowires. The magnetic and structural properties of the synthesized and commercial nanowires polarized by a magnetic field in the epoxy matrix were studied using the resonant radio-frequency magnetometry and electron microscopy methods. These methods are of interest for optimizing the coercive force of cobalt nanowires with a view to their possible use in creating permanent magnets that do not use rare earth elements, as well as in information processing devices and sensors.

Keywords-nanomagnetizm; electroless synthesis; cobalt nanowire; magnetometry

I. INTRODUCTION

The formation of one-dimensional nanostructures such as nanowires has attracted considerable attention due to their large anisotropic surface magnetism for practical applications, among them for the use in the fabrication of permanent magnets without rare-earth elements, memory devices, sensors, medical hyperthermia, and others [1-4]. High magnetization cobalt could become an ideal hard magnetic material if it could be prepared in the form with a large shape anisotropy. The use of template electrodeposition to produce the oriented magnetic nanowires of the controlled diameter and length [5] is complicated by the preparation of templates and the subsequent removal of nanowires from them. Applying magnetic fields in the reduction of solutions, i.e. hydrothermal and solvothermal synthesis, used to produce one-dimensional Co nanostructures

[6], requires high temperature, high pressure, and long reaction times. In this paper, we present a simple and effective low-temperature chemical method that provides the synthesis of nanowires due to the processes of self-organization of magnetic cobalt nanoparticles under the influence of a magnetic field, using the technology of electroless synthesis of magnetic nanoparticles and nanowires [7-10].

Cobalt nanoparticles have magnetic dipole moments. An external magnetic field forces them to orient themselves parallel to the magnetic field. Dipole-dipole interactions between magnetic nanoparticles lead to the attraction between cobalt nanoparticles leading to their self-organization into nanowires, reducing their total energy. The resulting smaller nanoparticles fill the gaps between the ordered nanoparticles, forming of smooth cobalt nanowires. Since the direct observation of magnetization reversal processes in the nanostructures of the magnetic nanopowder systems is hard to achieve, magnetoresistance measurements were used as an indirect sensing tool in [11] and the individual Co nanowires were prepared by electron beam lithography. Nonmagnetic gold contacts were attached to the Co nanowires to eliminate the influence of the contact structures on the magnetization reversal process. Depending on the direction of the applied field three different magnetoresistance measurements were distinguished: in plane parallel and antiparallel to the axis of the wire, called the longitudinal direction, and in plane perpendicular to the axis of the wire, the so-called transversal direction. The clear correspondence of the magnetoresistance, to the magnetization reversal was demonstrated. The magnetoresistance shows a hysteretic behavior with pronounced minima marking switching fields, which are identical to the coercive fields. Authors in [9, 10] demonstrated for the first time the possibility of measuring the degree of Domain Wall (DW) pinning in cobalt nanowires using the NMR method under the influence of an additional magnetic video-pulse. The DW pinning force in nanowires turned out to be of the order of 100 Oe and higher. Therefore, the coercive force of cobalt nanowires, or the magnitude of the external magnetic field required to reverse the magnetization of nanowires pre-polarized in a magnetic field, is expected to be close to the DW pinning force in these nanowires. Since the residual magnetic field of the iron cores of the electromagnet turned out to be about 200 Oe, the Helmholtz coils were used to measure in the required range of the external magnetic field from 0 to 200 Oe. The process of nanowire magnetization reversal was studied for three cases: in the case of an increase in the magnetic field along the nanowire magnetization and the opposite direction, as well as in the case of a direction transverse to the nanowires.

In the present work, the magnetization reversal processes of synthesized and commercial cobalt nanowire arrays, polarized by the external magnetic field in an epoxy matrix, are studied for the first time using the non-contact method of resonant Radio-Frequency (RF) magnetometry, similar to that used in [12, 13].

II. EXPERIMENTAL PROCEDURE

An improved version of the electroless chemical method [9, 10] was developed for the synthesis of Co nanowires. This method involves isolating cobalt metal from a chemical solution (Figure 1(a-e)) placed between the poles of a permanent magnet (Figure 1(f)). This is a simple and inexpensive method that does not use expensive catalysts.

In the next step, to obtain cobalt nanowires, the same solution (heated to 80 °C) was placed between the poles of a magnet (Figure 1(f)) where cobalt nanowires began to form. It is advisable to apply a surfactant to the surface of the solution so that the separated cobalt nanowires do not agglomerate.

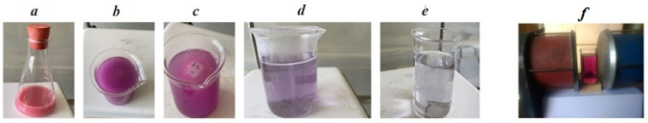


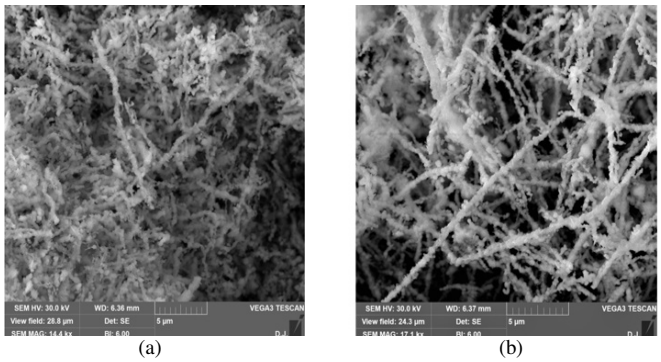
Fig. 1. Electroless chemical synthesis dynamics (a-e) and experimental set-up (f) for cobalt nanowire synthesis.

The method used in this work for synthesizing cobalt nanowires is based on their formation from a chemical solution when placed between the poles of a permanent magnet. The reagents used in the experiment are of the analytical grade. In particular, we prepare a solution of the following composition: $CoSO_4 \cdot 7H_2O$ -10 g/l; $KNaC_4H_4O_6$ $4H_2O$ – 40 g/l; N_2H_4 H_2O - 50 ml/l; NaOH ≈ pH 13, where the main source of cobalt ions is its salt, and sodium potassium tartrate $KNaC_4H_4O_6$ $4H_4O$ acts as a complexing agent that determines the stability of the solution and the hydrazine hydrate N_2H_4 H_2O is a reducing agent which defines the process of releasing cobalt ions in metallic form. The participation of a surfactant in this process is also important. For this aim toluene was used, which promotes the separation of cobalt ions reduced in solution, preventing their agglomeration. To obtain a cobalt nanopowder, a complexing agent was first added to a cobalt salt solution, and then hydrazine hydrate, resulting in the color of the solution becoming pale pink and cloudy (Figure 1(a)). At this point, the measured pH of the solution was 11. Then the NaOH solution was added until the solution was completely transparent (pH = 13), and then the solution was heated up to 75-80 °C. A surfactant had to be added to the solution (Figure 1(b)) to prevent agglomeration of the released particles of metallic cobalt. At 75 °C, the first particles of metallic cobalt emerged from the solution (Figure 1(c)). The intensity increased at 80 °C and the solution was placed on an electric furnace outside the magnet. Using toluene, cobalt particles rising to the surface of the chemical solution were periodically removed from the solution with a magnet and the solution was returned to the furnace. NaOH was periodically added to the depleted solution (Figure 1(d)) (up to pH-13), which ensures complete depletion of the solution in Co particles. The solution became colorless and transparent (Figure 1(e)). The total amount of NaOH used in this solution was about 10 g/L.

After the formation of cobalt nanowires began, the resulting nanowires were removed on average once every 2 min, and the cobalt solution was returned to its original position between the poles of the magnet. As the pH of the solution decreased, the rate of formation of cobalt nanowires decreased correspondingly, therefore, the addition of NaOH maintained a high pH until the solution became completely colorless. The

duration of the process determines the size of the resulting nanowires. The nanowires were separated from the solution with a magnet. They were then washed with alcohol using an ultrasonic device. In addition to the duration of the synthesis reaction, the thickness and length of cobalt nanowires were affected by the concentration of the reducing agent and the magnitude of the external magnetic field.

Figure 2 shows the electron diffraction patterns of synthesized and commercial samples of cobalt nanowires obtained using the SEM TESCAN VEGAS XMU scanning microscope. A cobalt nanowire from PlasmaChemGmbH with an average diameter of 200-300 nm and a length of up to 200 μm was used. The average diameters of both types of nanowires are close, but the average length of the synthesized nanowires is approximately 5 times shorter. Cobalt nanopowders were synthesized under the same conditions as nanowires, except for the presence of an external magnetic field. Next, epoxy capsules with cobalt nanowires and nanopowders were produced. The nanowires obtained as a result of the experiment were placed in a polyethylene tube with epoxy resin. In particular, a transparent polyethylene tube with a length of 3 cm and an internal diameter of 6 mm was used. The tube was closed on one side with a silicone plug (5 mm long) and the required amount of cobalt nanowire was placed in it (in our case 0.4 g) and epoxy resin was added to form a 2 cm long capsule. Then the liquid epoxy resin was mixed in the capsule using a small wooden stick until a homogeneous suspension of cobalt nanowires was obtained. Finally, the capsule was closed with a silicone plug and placed between the poles of a magnet for 1 day until the epoxy resin was completely cured. Next, the direction of the magnetic field on the resulting capsule was noted and examined. After hardening, the polyethylene shell can be removed from the sample and further research can be carried out.



(a) (b)

Fig. 2. The electron diffraction patterns of the synthesized (a) and commercial (b) cobalt nanowires.

To characterize the magnetic properties of the received nanowires the home-made Radio-Frequency Resonant Magnetometer (RF RM) was used, which allows assessing more quickly the magnetic state (ferromagnetic, superparamagnetic) of the test sample compared to relatively long-term measurements using the VSM magnetometry method [13].

The circuit based on the LC resonant generator (Figure 3(a)) was used to measure the transverse susceptibility of magnetic samples. The sample was placed into the induction coil of the LC generator. The changes of its resonance frequency were measured by changing the external magnetic field H_{DC}, perpendicular to the field of the RF coil. The standard representation of the frequency of the LC generator oscillations is:

$$f = \frac{1}{2\pi\sqrt{LC}}$$

where L is the inductance of the coil and C is its capacity.

Introducing the sample into the induction coil changed the inductance value by ΔL. If $\Delta L/L << 1$, by differentiating this equation, we get:

$$\frac{\Delta f}{f} = -\frac{\Delta L}{2L}$$

Changes in inductance are associated with the changes in the magnetic susceptibility of the studied magnetic nanopowders.

Figure 3(b) shows the experimental set up picture. Figures 4 and 5 show the dependences of the resonance frequency change Δf (H) under the influence of magnetic field (the resonant frequency f_0 = 10 MHz in the absence of magnetic field) for samples using commercial and synthesized nanowires, correspondingly.

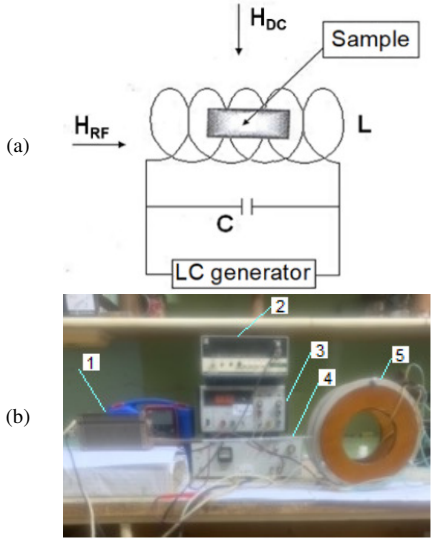


Fig. 3. (a) Schematic diagram of an LC generator, (b) the experimental set-up: 1. LC – generator, 2. frequency meter, 3. current source, 4. universal power supply, 5. Helmholtz coils.

Figure 6 shows a typical hysteresis dependence of the change in the resonant frequency of an LC-generator Δf (H) under the influence of a longitudinal external magnetic field. It can be seen that the dependence Δf (H) passes through a negative minimum at a value of H close to the magnetization

reversal field H_c and coincides with the coercive force of the cobalt nanowires.

It is interesting to compare the obtained hysteresis dependence $\Delta f\,(H)$ of cobalt nanowires in Figure 6 with similar data on the effect of magnetization reversal of thin Co nanowires obtained by electron beam lithography on their longitudinal magnetoresistance (Figure 7) [11]. It can be seen that the resistance passes through clearly defined minima at values of the longitudinal magnetic field close to the coercive field H_c.

The change in the resonant frequency of the RF resonant magnetometer depending on the applied external magnetic field characterizes the magnetic susceptibility change of a sample related to the DWs displacement under the influence of the external magnetic field. Typical dependences of susceptibility on the external magnetic field show characteristic peaks associated with the process of the sample magnetization reversal.

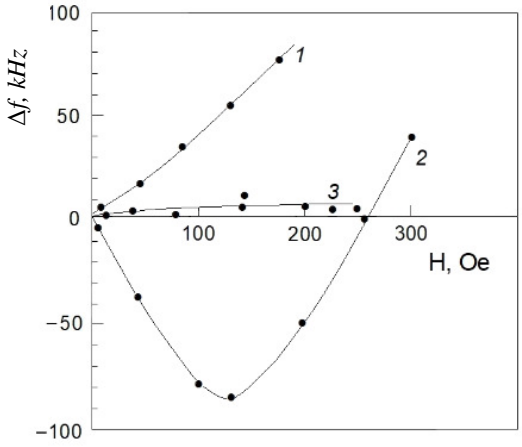


Fig. 4. Change in the resonant frequency $\Delta f\,(H)$ of the commercial Co nanowires: 1. magnetic field H increases along the magnetization direction, 2. magnetic field increases in the opposite direction, 3. magnetic field increases in the perpendicular direction to the nanowires.

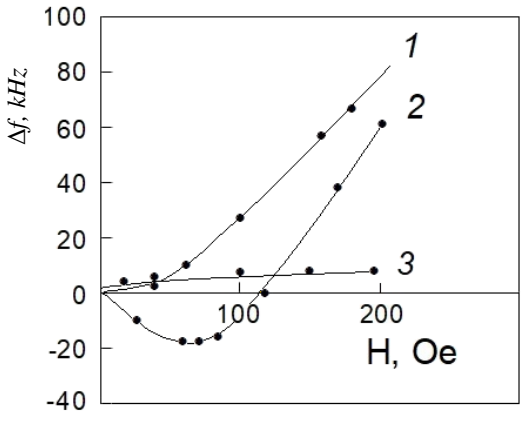


Fig. 5. The $\Delta f\,(H)$ dependence for the synthesized nanowires: 1. along and 2. in opposite direction to the magnetization of the Co nanowire, and 3. magnetic field directed in perpendicular to the synthesized nanowire.

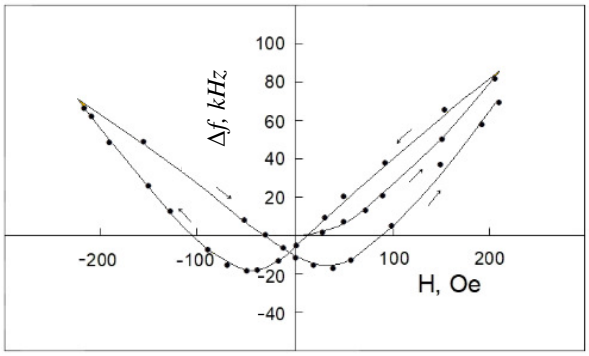


Fig. 6. Hysteresis curves $\Delta f\,(H)$ of the synthesized nanowires. A magnetic field was directed along the nanowires.

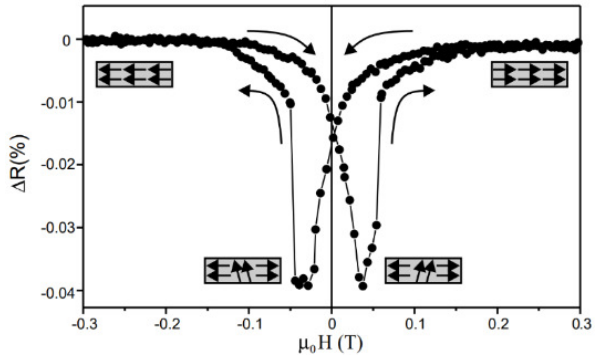


Fig. 7. Longitudinal magnetoresistance of a Co nanowire (width = 529 nm, T = 4.2 K). The relative resistance value is shown relative to the saturation value [11].

III. CONCLUSIONS

A simple and effective low-temperature electroless chemical method that provides the synthesis of cobalt nanowires due to the processes of self-organization of magnetic cobalt nanoparticles under the influence of a magnetic field, using the technology of chemical synthesis of magnetic nanoparticles and nanowires was proposed in this paper.

To carry out the comparative study of the coercive forces of synthesized and commercial cobalt nanowire arrays polarized by an external magnetic field in the epoxy matrix, a non-contact resonant radio-frequency magnetometry method was developed for the first time. An accurate assessment of the coercive forces in cobalt nanowires, combined with improvements in the method of their synthesis, makes their use promising for the manufacture of permanent magnets without rare earth elements, memory devices, or sensors.

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