



Research articles

Magnetic reversion in real nickel and cobalt nanowires and the angular dependence of coercivity

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ABSTRACT

Using micromagnetic simulation we present an analysis about the effects of the microstructure on the angular dependence of coercivity and quadrature. The results return curves profiles that resemble experimental data already reported in the literature. We show that, there is an ambiguity in case of adopting the curve profile of the angular dependence of coercivity as the starting point to assume the predominant reversion mode. We conclude in this study that, to infer any reversal mechanisms always have to take into account the nanowires microstructure.

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1. Introduction

Many papers have reported studies about the properties of nanowires arrays deposited on porous membranes [1–3]. Most are focused on the magnetic behaviors as a function of nanowires diameter, the distance between them and some works have based on the effects of length. There are several preparation routes using alumina membranes [1–5]. Each preparation method determines the internal microstructure that differs in polycrystallinity, orientation and shape of the crystals constituting the nanowires, etc. [6,7]. Recent works discussed the different types of magnetization reversal process, depending on the angular dependence of coercivity for Co-Cu segmented nanowires fabricated in alumina membranes [8,9]. Our previous works present analytical models based on chains of ellipsoids to somehow represent the actual nanowires structure and try to describe the properties for these systems looking at their structure [10,11]. In these works we argue the structure with a very simple model in which the wires are conformed by ellipsoids and located equidistant, as well as neglecting the crystalline structure. The models presuppose coherent reversal of magnetic moments to facilitate the final analytical results. These conditions are not real and so we use in other paper the micromagnetic simulation to try to describe in a more adequate way the properties related to the angular dependence of the coercivity and remanence [12,13]. In the simulations we used two microstructures of nanowires; conformed by ellipsoids and

cuboctahedrons. These proposals were based on transmission electron microscopy observations showing the real nanowires. Another kind of micromagnetic simulations including temperature and using Monte Carlo method in arrays of magnetic nanowires have been done to explain the realistic properties of these systems [14,15]. Some studies related the effects of the thermal treatment on the magnetic properties, increasing the coercivity and the effective field of the nanowires [7,10,11].

Even this, no many detailed studies were done on the effects of heat treatment on electrodeposited nanowires. Based on all this, and knowing that thermal treatment radically changes the atomic structure of the wires, the idea arises of generating hysteresis curves using numerical simulation to verify the effects of the structural changes. Once this, compile data on angular dependence of coercivity and remanence to verify the profile of the curves and compare with those presented in the experimental works existing in the literature. We know that the shape of curves of this type has been frequently used to be associated with the reversal mode of magnetization in nanowires arrangements. The present work shows the effects of the microstructure on the angular dependence of magnetization and coercivity by using micromagnetic simulation. The great novelty of the work is to show that, the shape of these curves is not enough to infer the reversal mode in the magnetization in electrodeposited nickel nanowires.

2. Method

We assume polycrystalline nanowires submitted to different times of thermal treatment. We know that real crystals begin to

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join by the effects of atomic diffusion, and then connected crystals soon after the treatment. In this way, if the treatment is extended, more crystals would be bonded and the nanowires microstructure would be even more affected. With these arguments and our previous papers, we propose the study by micromagnetic simulation for polycrystalline samples with crystals in cuboctahedral format in three situations; without treatment (Polycrystalline nanowire) and with short thermal treatment (Thermal treatment 1) and longer (Thermal treatment 2). This would generate the samples shown in Fig. 1a. Considering polycrystalline nanowires formed by ellipsoids, we also propose the study of two other samples; untreated and treated, Fig. 1b. In the literature several crystal geometries are reported, from transmission electron microscopy results. Our previous work shows wires with ellipsoidal and polyhedral crystals [10–13]. For materials with cubic structure the geometry of the crystals is the result of energy competitions during the formation of the wire. It is difficult to meet all geometries, sizes, crystal orientations, etc. but as our central idea is to show that, the microstructure is determinant in the angular dependence of coercivity and remanence; we studied ellipsoids and cuboctahedrons.

In the experiments, the nanowires are normally studied forming hexagonal arrangements and several lengths, and then we assume nanowires with lengths of 460 nm, Fig. 2a. The center-to-center

interwires distance was set at 70 nm and the mean diameter of 30 nm like the electrodeposited in anodic alumina membranes, Fig. 2b. The crystals in the nanowires do not have the same crystallographic orientation, i.e. the crystalline axes of each nanocrystal in the nanowire are randomly oriented for reproducing a realistic situation.

Calculations of hysteresis loops (M-H), were performed by micromagnetic simulations with the public domain package NMAG [16]. The code uses a hybrid finite element/boundary element method approach. The M-H data were computed for different direction (angle) of application of the external magnetic field, relative to the wire axis. Starting from positive saturation (external magnetic field of 3000.0 Oe) decreasing in a step of 60 Oe until the negative saturation (−3000.0 Oe) to complete a full cycle. Two materials were analyzed; nickel and cobalt. It is because nickel present cubic magneto-crystalline anisotropy and cobalt axial magneto-crystalline anisotropy. The inclusion of the two representative materials is justified because the great number of papers reporting magnetic properties in nickel and cobalt nanowires. The bulk nickel magnetic parameters $K_1 = 85700 \text{ J/m}^3$, $A = 9 \times 10^{-12} \text{ J/m}$ and $M_S = 4.9 \times 10^5 \text{ A/m}$, were extracted from [13]. The typical magnetic parameters for cobalt were used [17,18]: saturation magnetization, $M_S = 1400 \times 10^3 \text{ A/m}$, exchange stiffness constant, $A = 30 \times 10^{-12} \text{ J/m}$ and magneto-crystalline anisotropy

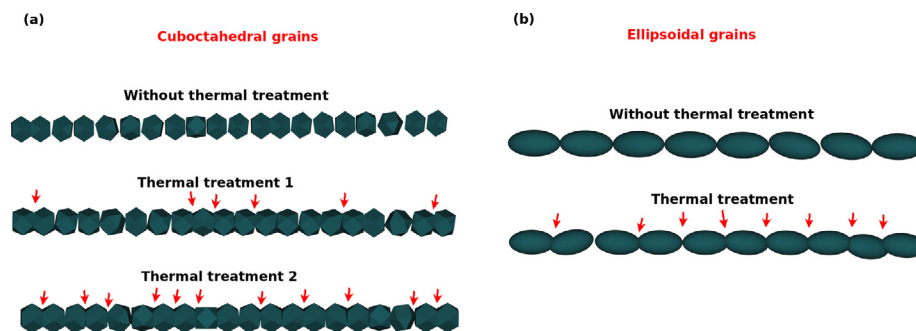


Fig. 1. Microstructure of the simulated nanowires. a) Octahedral geometry with nanocrystals unconnected (samples without thermal treatment), connected crystals as a short thermal treatment and the long treatment conditioning more connected crystalline structure. b) Ellipsoidal crystalline format with and without thermal treatment.

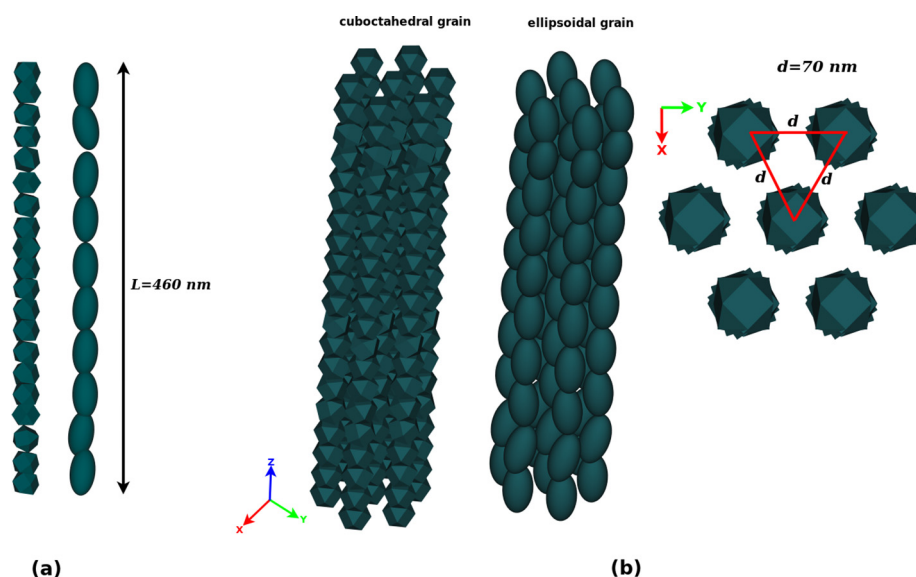


Fig. 2. a) Scheme showing wires formed by nanocrystals in ellipsoidal and cuboctahedral form. The crystal chain forming a nanowire length of 460 nm. b) The arrangements studied in this work were formed by polycrystalline wires in hexagonal order with center-to-center distance of 70 nm and diameter of 30 nm.

constants $K_u = 400 \times 10^3 \text{ J/m}^3$. The meshes have been created using NETGEN [19]. The geometry was divided into tetrahedral cells with edge average length smaller than the exchange length, 7.72 nm for nickel and 4.9 nm for cobalt [13,18].

3. Results

To organize the discussion, we began by analyzing the results concerning nickel nanowires. In Fig. 3a the magnetization curves generated applying parallel field related to the wires axis are shown. Nanowires are constituted by cuboctahedral nickel crystals and different morphologies according to long and short thermal treatment, Fig. 1. The hysteresis cycle becomes wider as the “treatment time” increase and “untreated” sample has a behavior that has been shown in many experimental studies [10–13]. The calculated loop is not to square due to the crystallinity and absence of strong exchange interaction between the crystals inside the wires structure. For nickel nanowires the predominant interaction would be dipolar and conditions a strong demagnetizing effect within each cuboctahedron. The cuboctahedral geometry presents flat faces in well defined directions and due to the reduced size of crystals, there will be a strong dipolar component, making the magnetization process difficult.

The “treated nickel nanowires” named as Thermal treatment 1 present pairs of nickel crystals connected at some locations of the wires, as shown in Fig. 1a. In this new situation (if compared to the untreated) the pairs of crystals participate as a single object with an elongated shape in 1:2 ratio along the nanowire. Thus, the

demagnetizing interactions along the nanowire decreases thus increase the effective field in this direction, which conditions the widening of the hysteresis loop. For the sample treated in an even longer time (Thermal treatment 2) the curve enlargement is high still because in this case we have a larger amount of coupled crystals forming a single object as represented in Fig. 1a. Overall, we can say that, there is an increase in coercivity and quadrature for thermally treated samples, which is expected in the experiments.

The results for nickel nanowires conformed by ellipsoids are presented in Fig. 3b, showing an apparently contradictory result in comparison to the experiments. The sample without heat treatment presents a more pronounced magnetization curve than the treated. The proposed untreated sample is formed by a sequence of unconnected 1:2 shaped ellipsoids, oriented along nanowire. Each ellipsoid acts independently with a marked anisotropy in the long axis direction. The present geometry has not flat surfaces like octahedron. The contradiction with the experiments is because the fabrication by electro-deposition will hardly have samples formed by ellipsoids of single size and disconnected. A real sample always have connected crystals with different orientations, affecting the reversion of the moments and consequently to the format of the hysteresis curve. Just observing the, Figs. 1b and 3b, we have a quadrature affected by the connection of the crystals and the coercivity value is higher for the “thermally treated” sample.

Now we will analyze the hysteresis curves obtained for arrangements of cobalt nanowires. The treated sample in this case refers to the equivalent of the longer treatment, Fig. 3c shows the behavior of field magnetization for disconnected crystals and for connected crystals (which would be caused by deposition of a heat

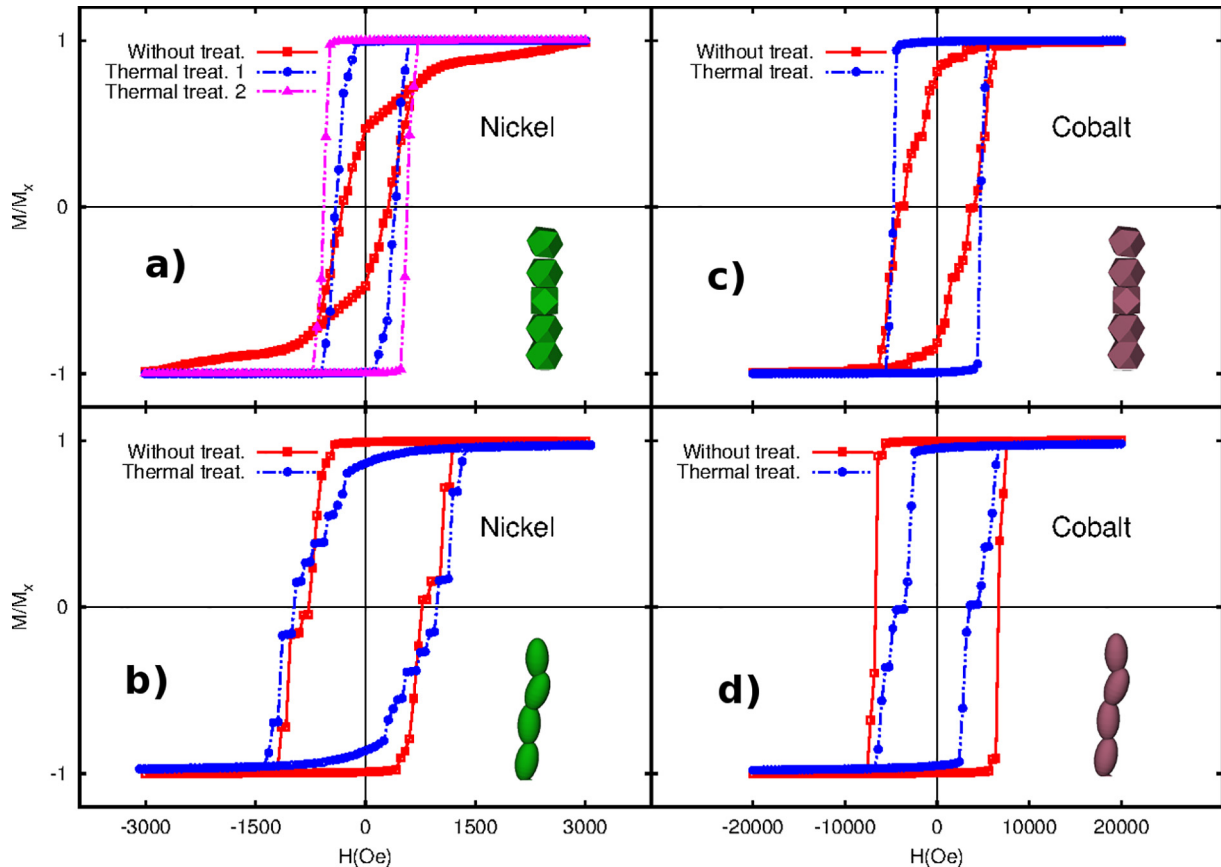


Fig. 3. a) Hysteresis curves for nickel nanowire arrangements with cuboctahedral crystals. The curves were calculated by means of micromagnetic simulation for wires with isolated crystals (sample without heat treatment) and with the crystals more and more glued, depending on the time of treatment. b) In this case we have nickel nanowires formed by ellipsoidal crystals. c) Hysteresis curves for cobalt nanowire arrangements with cuboctahedral crystals. d) Cobalt nanowires formed by ellipsoidal crystals.

treatment). The first aspect to be highlighted is that samples with connected crystals present a hysteresis loop similar to those reported in experimental studies in the literature [8,9]. It is also worth mentioning that the sample without heat treatment or with disconnected crystals presents with a hysteresis loop that has also been presented in articles [10–13]. The other result here to be taken into account is the large difference between the coercivity values when comparing the results for nickel in Fig. 3a and for cobalt in Fig. 3c. The high value presented by the cobalt samples can be easily explained by the average direction of the axis of easy magnetization caused by the magneto-crystalline anisotropy that is added to the auto-demagnetizing effect along the wires. In analyzing the results presented in Fig. 3d for nanowires with ellipsoidal crystals we can verify a combination of effects. First, the high values of coercivity due to the composition of the nanowires. On the other hand, when we compared the samples with connected crystals (heat treated sample) and disconnected, we can verify the same behavior observed in Fig. 3b, where there is a decrease in coercivity due to the possible formation of domain walls for glued crystals and giving lower values of coercivity. From a preliminary conclusion, we shall now say that the quadrature of hysteresis laces can hardly be attributed to a mode or other mode of reversal of moments. This is because in analyzing the curves presented here, we have several loop formats that originate in crystals of different shapes and that will not necessarily have similar

behavior to that already known for perfect cylindrical wires traditionally taken into account to analyze this type of systems.

The exploratory analysis with field applied in only one direction can give an idea of the most significant differences for each situation. The traditional experimental analysis for determining the reversal mode is realized by means of the coercivity and quadrature in different angles of applied magnetic field. We show in Fig. 4a the dependence of remanence as a function of angle for samples conformed by cub-octahedral crystals. The quadrature always has values below 0.5 for “untreated sample”. Many reported results are compatible with this behavior, especially nanowires of length lower than 1 micrometer, obtained using nitrates as precursors in the deposition bath. For these experimental results the crystals have a rounded format [4,5,7,10], different to the simulated in Fig. 4a. For the “thermally treated” nanowires there is no difference in results for Thermal treatment 1 and Thermal treatment 2. The collected data from a hysteresis loop is a summation of many effects and can hardly be associated to a single cause. That is, there may be diverse mechanisms leading to the profile of remanence dependence on the angle of application of the field.

In Fig. 4b we can verify the curve now calculated in arrangements of wires formed by ellipsoidal crystals. The profile corresponding to “untreated sample” reproduce the expected results in which moment reversal is in the coherent mode. It is

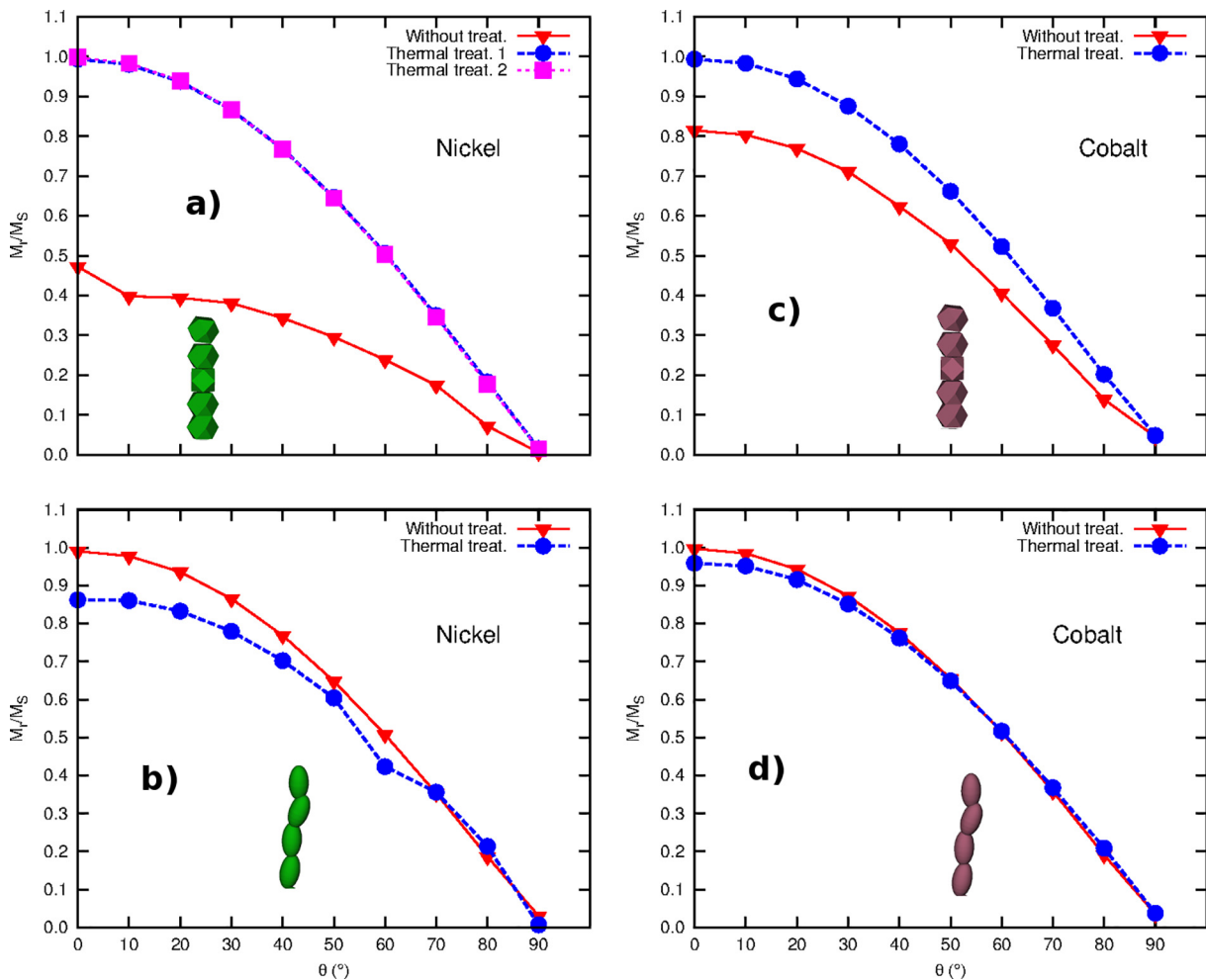


Fig. 4. a) Angular dependence of the remanence for nanowires formed by cuboctahedral crystals of nickel. Each curve represents a sample depending on the treatment time or, otherwise, how much the crystals are within the wire. b) The nickel nanowires are conformed by ellipsoidal crystals. c) Remanence for cobalt nanowire arrangements with cuboctahedral crystals. d) Cobalt nanowires formed by ellipsoidal crystals.

noteworthy that this curve resembles the resulted in Fig. 4a, corresponding to “heat treated” samples with cuboctahedral crystals. In other hand, the treated sample (ellipsoid), presents a behavior that would seem to contradict the experimental expected one. That is, one would expect that, after a “heat treatment” the quadrature would increase and therefore the dependence would not be like that obtained in Fig. 4b. After a heat treatment the crystals can stick together at the time of moment reversion; the coherent mode would cease to be predominant. Applied field at 60 degrees produces a small jump, suggesting a reversal regime changing. Looking at results in Fig. 4, for remanence as a function of the applied field angle, not always the treatment would increase the quadrature. Depending on the real nanowires micro-structure, many different results can be obtained. This leaves more evident than the study of global magnetic properties, without taking into account the actual crystalline structure of the wires, will never yield reliable results on how the modes of reversion manifest.

Reviewing now the curves generated for cobalt nanowires shown in Fig. 4c and d, we can see very differently to those already seen in the samples of nickel nanowires of Fig. 4a and b. For non-heat treated cuboctahedral crystals we can verify that the quadrature for parallel field is 0.8, much smaller than for the sample with connected crystals. The value mentioned here is due to the dipole interaction between the faces of highly symmetric crystals. The difference between the values for nickel and cobalt cuboctahedrons is

related to the strong influence of magneto-crystalline energy in this direction [4,5,13]. When we compare the curves for ellipsoidal crystals we see again a combination of effects. Disconnected ellipsoids present quadrature larger than the ones connected due to the size of these objects combined with the possibility of forming domain walls in connected crystals. On the other hand, the difference is not as high as for nickel ellipsoids; this is due to the effects of magneto-crystalline energy along the axis of symmetry of the wires.

Several experimental studies present the behavior of coercivity as a way of suggesting the predominant mode for magnetization reversion [20–24]. It is not entirely correct to base such arguments on how to reverse the moments in the material. As shown in some works, the most expected modes in cylindrical structures are the coherent, the vortex and the transverse for cylindrical geometry [25,26]. Each mode type returns a typical characteristics behavior for the angular dependence of coercivity, but this does not mean that a given behavior is strictly generated by a unique mode of magnetic reversal. Always is presented the profile of the curve and along with this the maximum and minimum values of the coercive field. A highly irregular shaped nanowire will hardly exhibit a cylinder-like moment configuration during all points of a magnetization curve. An irregular polycrystalline nanowire can generate angular dependencies of coercivity, compatible with those presented by perfectly cylindrical wires. Fig. 5 shows the

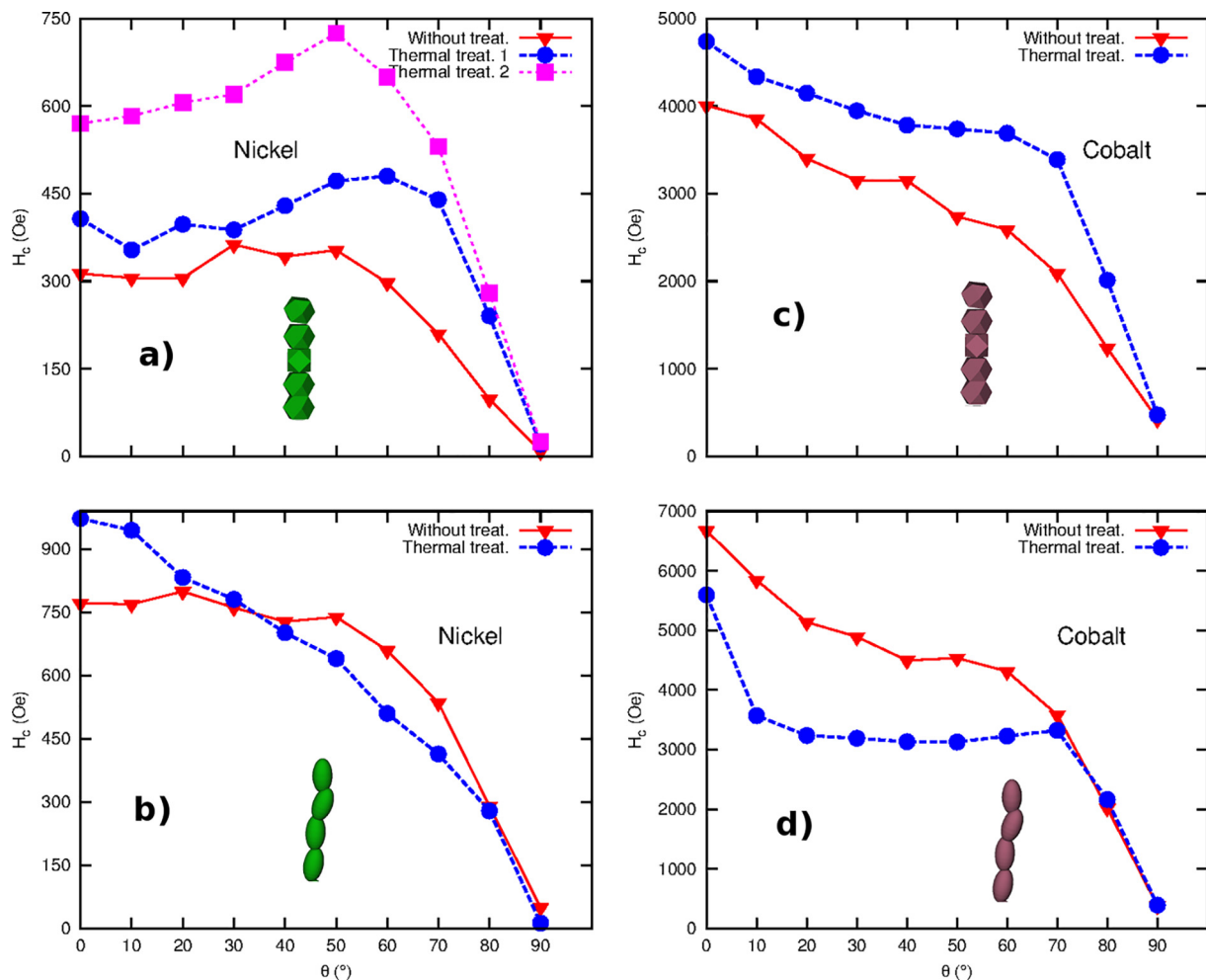


Fig. 5. a) Angular dependence of the coercive field for wires formed by cuboctahedral crystals. Each curve represents a sample depending on the treatment time or, otherwise, how much the crystals are within the wire. b) Nanowires are conformed by ellipsoidal crystals. c) Coercivity for cobalt nanowire arrangements with cuboctahedral crystals. d) Cobalt nanowires formed by ellipsoidal crystals.

angular dependence for the coercivity in wires ordered hexagonally and formed by cuboctahedral and ellipsoidal crystals. In each case we studied the samples treated and not treated thermally.

As a way of understanding how the microstructure determines the modes of magnetization reversal, some works already mentioned above, propose models for the effective field in the arrangements of nanowires in porous membranes. These models take into account the shape of the wires as perfect cylinders and others suggest ellipsoid chains. Besides that, when it comes to suggesting magnetic energy, a predominant mode is always previously assumed, which usually conforms to the shape of the coercivity field curve as a function of the angle of application of the external field. In the curves presented in Fig. 5 we can verify formats that could suggest vortex or transversal modes. We know this is not true because our data are the results of a micromagnetic simulation for crystalline structures that do not present these modes as solution, due to the great irregularities of the wires suggested here, Fig. 1. Some experimental data correspond to our results in Fig. 5a [12,13] and do not results from any of the reversion modes for cylindrical nanowires. In this way there is an ambiguity in case of being suggested the way of reversion starting from the profile of the angular dependence of coercivity and remanence. Looking at Fig. 5b, we also have some results already reported. The suggested format of perfect unconnected ellipsoids, proposed here, is not even close to the realization of real nanowires. Clearly, any kind of proposal about reversal mode is not possible because the diminution of coercivity and remanence values are suited to the lengths of the nanowires but also, strongly connected to the actual microstructure of each sample. In Fig. 5a the values double for the heat treated sample, that is, joining crystals inside the wires we have great changes. In Fig. 5b the results are more worrisome, because an experimental measure could suggest that sample after thermal treatment undergoes oxidation or another effect that we know in our case, with data that comes from numerical simulation, they do not exist. In general, we can see how different microstructures can present solutions for the micromagnetic equations that return diverse hysteresis loops. Thus, within the many factors that determine the angular dependence of coercivity and remanence, it is of great importance to make micro-structural studies before suggesting any mode for the magnetization reversal.

Fig. 5c and d are showing the surprising result that strongly resembles the curve profile of the angular dependence of coercivity when reversion occurs in the coherent mode. Note that for cuboctahedral-shaped crystals of cobalt there is a similar dependence already reported in the literature on experimental results [27]. The similarities are mainly due to the strong effect of magneto-crystalline energy which generates an overall effect on each particle, resembling a well-defined moment within each crystal. Attempts to successfully describe the behavior of magnetic nanowires have been present in the literature in recent decades and the conditions imposed by reality have been an obstacle to well understood experimental results [2,10,27]. Recently, Barriga-Castro et al. [28] reported the difficulty of precise determination of the real microstructure of magnetic nanowires through Transmission Electron Microscopy technique. It is due to the frustration mechanism occurred during the confined growth of the electrodeposited nanowires inside the pores of the anodic alumina templates, which induces the appearing of stacking faults and defect

in the structure of nanowires, leading to an imprecise or confusing determination of correct crystalline phase of the nanowire.

4. Conclusions

We finally conclude that, the profile of the angular dependence of coercivity and remanence cannot be used as a absolute way of inferring which mode of reversion predominates in real nanowires. In order to suggest a specific mode, it is necessary to have knowledge about the microstructure of the measured real nanowires array, using techniques such as transmission electron microscopy and X-ray diffraction.

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