

Large magnetic anisotropy enhancement in size controlled Ni nanowires electrodeposited into nanoporous alumina templates

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 Nanotechnology 27 145702

(<http://iopscience.iop.org/0957-4484/27/14/145702>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 132.248.12.211

This content was downloaded on 06/06/2017 at 18:52

Please note that [terms and conditions apply](#).

You may also be interested in:

[Enhanced magnetocrystalline anisotropy of Fe₃₀Co₇₀ nanowires by Cu additives and annealing](#)
Ester M Palmero, Ruslan Salikhov, Ulf Wiedwald et al.

[The role of the crystal orientation \(c-axis\) on switching field distribution and the magnetic domain configuration in electrodeposited hcp Co–Pt nanowires](#)
Muhammad Shahid Arshad, Mariana P Proenca, Spela Trafela et al.

[Control of the c-axis orientation in Co nanowires](#)
Michaël Darques, Armando Encinas, Laurent Vila et al.

[Magnetic hardening of Fe₃₀Co₇₀ nanowires](#)
Sara Liébana Viñas, Ruslan Salikhov, Cristina Bran et al.

[Control of the structure of CoCu nanowires arrays](#)
Michaël Darques, Anne-Sophie Bogaert, Fanny Elhoussine et al.

[Developing high coercivity in large diameter cobalt nanowire arrays](#)
A H Montazer, A Ramazani, M Almasi Kashi et al.

[Configuration dependent demagnetizing field in assemblies of interacting magnetic particles](#)
J M Martínez-Huerta, J De La Torre Medina, L Piraux et al.

[Thickness dependence of the magnetic anisotropy and dynamic magnetic response of ferromagnetic NiFe films](#)
E F Silva, M A Corrêa, R D Della Pace et al.

[Ferromagnetic resonance in Mn₅Ge₃ epitaxial films with weak stripe domain structure](#)
R Kalvig, E Jedryka, P Aleshkevych et al.

Large magnetic anisotropy enhancement in size controlled Ni nanowires electrodeposited into nanoporous alumina templates

J De La Torre Medina¹, G Hamoir², Y Velázquez-Galván³, S Pouget⁴,
H Okuno⁴, L Vila⁴, A Encinas³ and L Piraux²

¹Instituto de Investigaciones en Materiales—Unidad Morelia, Universidad Nacional Autónoma de México. Antigua Carretera a Pátzcuaro No. 8701 Col. Ex Hacienda de San José de la Huerta, C. P. 58190, Morelia, Mexico

²Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain. Place Croix du Sud 1, B-1348, Louvain-la-Neuve, Belgium

³División de Materiales Avanzados, Instituto Potosino de Investigación Científica y Tecnológica, A. C., Camino a la Presa 2055, 78216 San Luis Potosí, SLP, Mexico

⁴Université Grenoble Alpes and CEA, INAC-SP2M, F-38000 Grenoble, France

E-mail: delatorre@iim.unam.mx

Received 7 December 2015, revised 1 February 2016

Accepted for publication 3 February 2016

Published 24 February 2016



CrossMark

Abstract

A large enhancement of the magnetic anisotropy of Ni nanowires (NWs) embedded in anodic aluminium oxide porous membranes is obtained as a result of an induced magnetoelastic (ME) anisotropy contribution. This unusual large anisotropy enhancement depends on the diameter of the NWs and exceeds the magnetostatic (MS) contribution. As a consequence, it leads to effective magnetic anisotropy energies as large as 1.4×10^6 erg cm⁻³, which are of the same order of magnitude and comparable to the MS energies of harder magnetic materials like Co NWs. Specifically, from ferromagnetic resonance experiments, the magnetic anisotropy of the NWs has been observed to increase as its diameter is decreased, leading to values that are about four times larger than the corresponding value when only the MS anisotropy is present. Our results are consistent with the recently proposed growth mechanism of Ni NWs that proceeds via a poly-crystalline stage at the bottom followed by a single-crystalline stage with texture [110] parallel to the axis of the NWs. A strong correlation between reducing the diameter of the NWs with the decrease of the length of the poly-crystalline segment and the enhancement of the effective magnetic anisotropy has been shown. Magnetization curves obtained from alternating gradient magnetometry experiments show that the average ME anisotropy results from the competition between the magnetic anisotropies of both crystalline segments of the NWs. Understanding the influence of size and confinement effects on the magnetic properties of nanocomposites is of prime interest for the development of novel and agile devices.

Keywords: nanowires, magnetoelastic, alumina porous membranes, ferromagnetic resonance, size reduction

(Some figures may appear in colour only in the online journal)

1. Introduction

Tuning magnetic properties of arrays of nanowires (NWs) embedded into a host non-magnetic template is of considerable interest for the development of novel devices based on magnetic

nanocomposites like bit patterned media for perpendicular magnetic recording [1, 2], microwave devices [3–8] and spin transfer torque devices [9–12]. Besides structural features, magnetization reversal processes and inter-element dipolar interactions, several recent reports show that the interaction

between the template and the nanoelements can also be used to modify the magnetic properties of nanocomposite materials. Recent advances on the control of magnetic properties of multiferroic/magnetolectric heterostructures and composites [13–16] have proven its potential for the development of novel and functional devices. For instance, an interesting material intended for the development of agile microwave devices operating at room temperature is based on a two phase nanocomposite material made of magnetostrictive NWs embedded in a piezoelectric porous membrane [13]. Other studies have reported on the influence of the host matrix made of different materials, as for instance polycarbonate [17–20] and porous anodic aluminium oxide (AAO) [21] membranes, on magnetoelastic (ME) effects in arrays of magnetic NWs at low temperature. However, since the physical mechanism of these ME effects is based on the thermal expansion coefficients mismatch between the host porous membrane and the metallic NWs, they cannot be exploited for devices operating at room temperature. These previous studies suggest that both, the host matrix material and the diameter of the nanowires are important parameters that have direct influence on the magnetic properties of these nanocomposites. Integrating and exploiting these properties in a material capable of operating at room temperature is desirable for the development of magnetically tunable agile devices.

In this work we present a study on the room temperature magnetic anisotropy of arrays of Ni NWs embedded in porous AAO membranes, which has been done by performing alternating gradient magnetometry (AGM) and ferromagnetic resonance (FMR) experiments. The magnetic anisotropy energy of these arrays of NWs exhibits an enhancement as large as $8.6 \times 10^5 \text{ erg cm}^{-3}$ that is even larger than the value due to the magnetostatic (MS) contribution ($\approx 5 \times 10^5 \text{ erg cm}^{-3}$). This energy enhancement corresponds to a confinement-dependent ME anisotropy contribution that strongly depends on the diameter and length of the NWs. The FMR measurements are consistent with the presence of a polycrystalline segment that appears during nucleation at the early growth stage, which is subsequently followed by an epitaxial growth along the crystallographic direction [110] which is parallel to its axis. As a reference, arrays of low diameter permalloy (Py: $\text{Ni}_{80}\text{Fe}_{20}$) NWs embedded in AAO membranes present no magnetic anisotropy enhancement, so its magnetic anisotropy simply corresponds to magnetostatic contributions. Since Py has no magnetostriction this result indeed corroborates the ME nature of the magnetic anisotropy enhancement observed in arrays of magnetostrictive Ni NWs. Furthermore, measurements of initial magnetization curves also allow to obtain the ME anisotropy contribution, which depends on the diameter of the NWs and is consistent with a competition between the corresponding energy excess of the two crystalline segments.

2. Experimental

Arrays of Ni and Py NWs have been fabricated by a standard three-probe electrodeposition technique. In this work we have

used commercial 50 and 90 μm thick AAO membranes from Synkera Technologies, Inc. with pores diameter (d) and porosity (P) in the ranges 18–100 nm and 10%–15%, respectively. A Cr(20 nm)/Au(600 nm) layer is evaporated onto one side of the membranes to serve as a cathode for the electrodeposition and as a ground plane for the FMR experiments. Ni and Py NWs are grown, respectively, from electrolytes with compositions $262.8 \text{ g l}^{-1} \text{ NiSO}_4 + 30 \text{ g l}^{-1} \text{ H}_3\text{BO}_3$ with the pH adjusted to 4; and $131.4 \text{ g l}^{-1} \text{ NiSO}_4 + 5.6 \text{ g l}^{-1} \text{ FeSO}_4 + 24.7 \text{ g l}^{-1} \text{ H}_3\text{BO}_3$ with the pH adjusted to 3. Electrodeposition is done in potentiostatic mode at room temperature by applying potentials of -1.05 V and -1 V for Ni and Py respectively. Arrays of Ni NWs with different lengths in the range 8–72 μm were fabricated by controlling the growth time. The lengths of the different arrays of NWs were confirmed by optical and scanning electron microscopy (SEM) observations. X-ray diffraction (XRD) measurements have been carried out for the determination of the crystalline structure of the NWs by using $\text{Co K}\alpha_1$ radiation of wavelength $\lambda = 1.79 \text{ \AA}$. Assuming that all the pores are filled electrochemically, the packing fraction of the array of NWs corresponds to the porosity of the membrane. For the characterization of the magnetic anisotropy of the arrays of NWs studied in this work, room temperature FMR and AGM experiments have been performed. FMR measurements have been done by using the microstrip transmission line method [22] and absorption spectra have been recorded in the field swept mode by applying the external DC field in the direction of the NWs axis in the range 0–10 kOe. The linear transmission coefficient $T = 10^{S/20}$ is obtained from the measured field swept insertion loss parameter S . It must be stressed that FMR measurements are done in the saturated state in order to make sure that the NWs are in the single domain regime. The fact that the aspect ratio of the NWs analyzed in the present study is larger than 10 means its critical radius is of about 600 nm, which further corroborates the single domain regime of the NWs [23]. AGM measurements in the field range $\pm 10 \text{ kOe}$ have been performed by recording both: hysteresis loops with the external field applied along their axis and initial magnetization curves after AC demagnetization in the directions parallel and perpendicular to their axis.

3. Results

The first evidence of a significant enhancement of the room temperature magnetic anisotropy of arrays of Ni NWs is observed from the FMR experiments. Figure 1(a) shows absorption spectra recorded at 27 GHz for arrays of Ni NWs with lengths between 28 and 40 μm and with diameters and packing fractions of 18 nm and 10% (dashed-dotted line), 35 nm and 12% (dotted line), and 100 nm and 15% (dashed line). The resonance field at the minimum of the absorption peak for the 100 nm diameter array of Ni NWs shown in figure 1 (a), lies very close to the upper field limit of the vertical shaded area corresponding to the resonance field $H_r^{[0]}$, which is due only to the MS anisotropy contribution and can

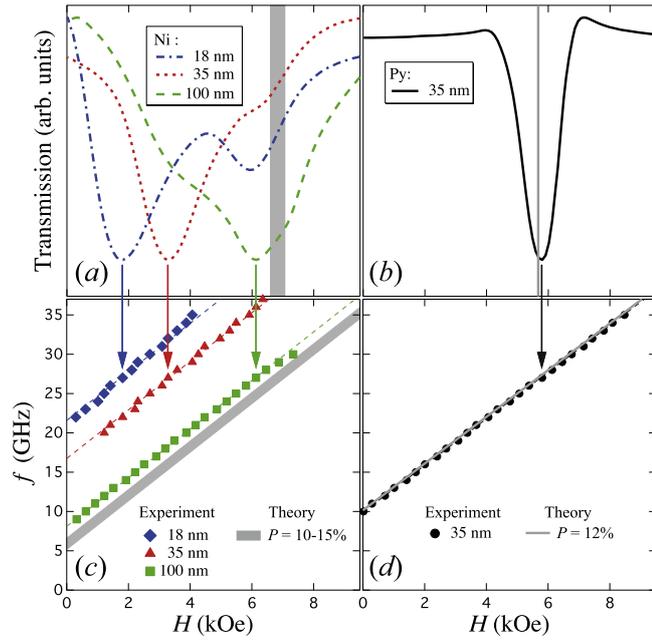


Figure 1. Room temperature absorption spectra recorded at 27 GHz for arrays of (a) Ni and (b) Py NWs. Ni NWs have d and P values of 18 nm and 10% (dashed–dotted line), 35 nm and 12% (dotted and continuous lines) and 100 nm and 15% (dashed line), whereas for Py NWs $d = 35$ nm and $P = 12\%$. The vertical line and shaded area, that accounts for variations of P , indicate the values of $H_r^{[0]}$ due only to the MS contribution (see equation (1)) for arrays of Py and Ni NWs, respectively. The dispersion relations for the samples considered in figures 1(a) and (b) are displayed respectively in (c) and (d). Dashed lines are linear fits and arrows indicate the resonance field for each dominant absorption peak. The gray line and shaded area correspond respectively to the dispersion relations for Py and Ni arrays of NWs that result from MS contributions.

be obtained from the resonance condition

$$\frac{f_r}{\gamma} = H_r^{[0]} + H_{ms}. \quad (1)$$

In this equation f_r is the resonance frequency, H_{ms} is the MS field including the shape and the dipolar interaction terms [22] given by

$$H_{ms} = 2\pi M_s(1 - 3P), \quad (2)$$

where $M_s = 485 \text{ emu} \cdot \text{cm}^{-3}$ and $\gamma = 3.09 \text{ GHz kOe}^{-1}$ are respectively the saturation magnetization and the gyromagnetic ratio for Ni. On the other hand, in the case of the 18 and 35 nm diameter arrays of Ni NWs their corresponding major absorption peaks are located at much lower resonance field values (≈ 1.8 kOe for the former and 3.5 kOe for the later) that clearly indicate that their effective anisotropies are larger than the one for the Ni NW array with $d = 100$ nm and particularly larger than the MS contribution. As a comparison, figure 1(b) displays the absorption spectra recorded at 27 GHz for an array of 35 nm diameter Py NWs, whose resonance field value corresponds to the expected value due to the MS contribution given by equation (1), with $M_s = 850 \text{ emu} \cdot \text{cm}^{-3}$ and $\gamma = 2.97 \text{ GHz kOe}^{-1}$ for Py. From figures 1(a) and (b), the resonance fields for the two arrays of Ni NWs with diameters of 18 and 35 nm are lower than

their expected values considering only the magnetostatic contribution using equation (1) (see the shaded area) and still lower than the resonance field for the Py NW array (vertical line). The shaded area in figure 1(a) accounts for the variation of P for the different arrays of Ni NWs, such that the lower the value of P the lower the resonance field. Therefore, the observed resonance field shift with respect to the shaded area of more than 5 kOe is larger than the MS field, $H_{ms} \approx 1.68 - 2.13$ kOe for P in the range 10%–15%. Although these arrays exhibit an additional anisotropy contribution of the same order of magnitude as that of the MS contribution, it can not be explained in terms of the magnetocrystalline anisotropy ($K_1 = -0.5 \times 10^5 \text{ erg cm}^{-3}$ and $K_2 = -0.2 \times 10^5 \text{ erg cm}^{-3}$) because it is negligible in comparison with the MS contribution at room temperature [24, 25]. The fact that Py has zero magnetostriction [18] reinforces the assumption that for low diameter arrays of Ni NWs the shift of the resonance field toward lower values from that of equation (1) must be the result of an additional size dependent ME anisotropy contribution. It must be stressed that the fabrication process and the FMR measurements in the present work have been carried out at room temperature.

From the global minimum of the absorption spectra recorded at different frequencies, the corresponding dispersion relation is obtained. Figures 1(c) and (d) show the dispersion relation for each of the samples considered in figures 1(a) and (b). The shift of the resonance field to lower values observed for the low diameter NWs in figure 1(a) corresponds to an upward shift of the resonance frequency, so that higher frequencies indicate a larger anisotropy energy. Particularly, the zero field resonance frequency for the 18 nm diameter NWs is about four times larger than the expected value due only to the MS contribution (see the shaded area), which means that in this case its magnetic anisotropy is dominated by an anisotropy contribution of ME origin that is clearly larger than the MS contribution. The shift of the absorption spectra toward lower values of the resonance field when decreasing d reveals that the magnetic anisotropy of Ni NWs is closely related to their size dependent-crystalline structure. That is, low diameter Ni NWs have preferential growth along the crystalline direction [110], whereas large diameter NWs have no preferential growth along a specific crystalline orientation as already reported [26–28].

The features observed in figure 1(a) are corroborated in our arrays of NWs with diameters of 18, 35 and 100 nm from the XRD patterns shown in figures 2(a)–(c). As seen in the figure, the crystalline structure of the 18 and 35 nm diameter NWs is well oriented along the [110] direction because only the peak corresponding to the (220) plane is visible. As the diameter increases to 100 nm, the peak for the (111) plane becomes more pronounced in comparison to the one for the (220) plane and peaks for other planes are now visible, revealing the polycrystalline feature of the NWs.

Besides the resonance field shift, the absorption spectra for the 35 nm diameter Ni NW array of figure 1 (a) displays a complex non-symmetric line-shape that is slanted and presents a shoulder besides the main absorption peak. Broad and asymmetrical FMR spectra can be regarded as the

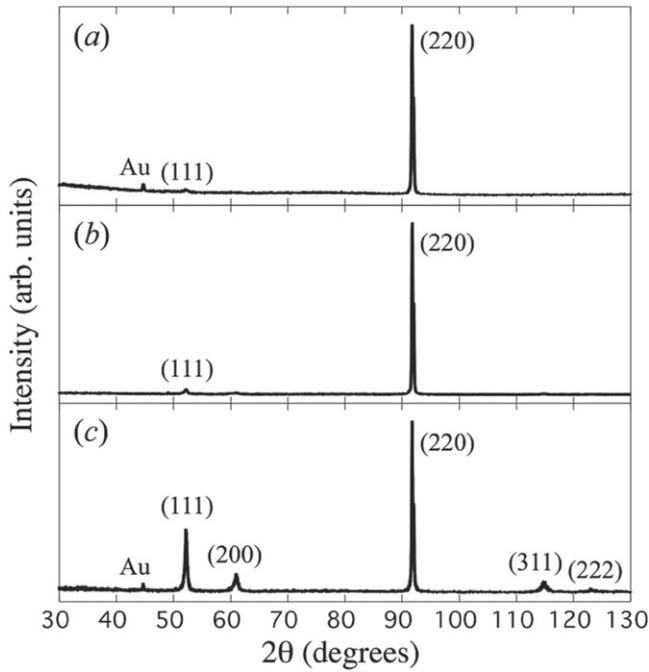


Figure 2. XRD patterns of arrays of Ni NWs with diameters of (a) 18 nm, (b) 35 nm and (c) 100 nm.

superposition of different absorptions. Such peaks can be interpreted as distributions of resonance fields, which in turn are associated to anisotropy distributions with a double peak line-shape. This feature indicates that the NWs present two different magnetic anisotropy distributions. Similar absorption spectra were already reported in the case of Co nanowires exhibiting different magnetocrystalline anisotropy contributions [29]. The asymmetrical feature of the absorption spectra and the presence of two main magnetic anisotropies is further evidenced as the length of the NWs is changed as observed in figure 3. This figure displays the normalized field sweep absorption spectra recorded at 30 GHz for 35 nm diameter Ni NWs with $P = 12\%$ and lengths of about 9% ($8 \mu\text{m}$), 19% ($17 \mu\text{m}$), 40% ($36 \mu\text{m}$) and 80% ($72 \mu\text{m}$) of the maximum attainable length corresponding to the membrane thickness ($\approx 90 \mu\text{m}$). The effect of the NWs length is further evidenced for arrays of NWs with larger diameters, as shown in figure 3 (b) from the comparison between the FMR spectra recorded at 27 GHz for the two arrays of 100 nm diameter NWs with lengths of 22 and $28 \mu\text{m}$. These changes are related to a complex growth mechanism of the NWs for which the crystalline structure along its axis changes during the growth. As reported in the case of Sb and Co [30], as well as Ni NWs [31, 32], an initial 3D nucleation mechanism is followed by a 2D epitaxial growth, leading to a change in the NWs structure from poly-crystalline to single-crystalline. Moreover, several reports have shown that these features depend on the diameter of the NWs [26–28]. Therefore long enough NWs have a two stage crystal growth as shown schematically in figure 3(c), where each crystalline segment presents a local magnetic anisotropy associated to one of the two absorption peaks in the spectra. The fact that the resonance field for both absorption peaks lie at lower field values than the one for the

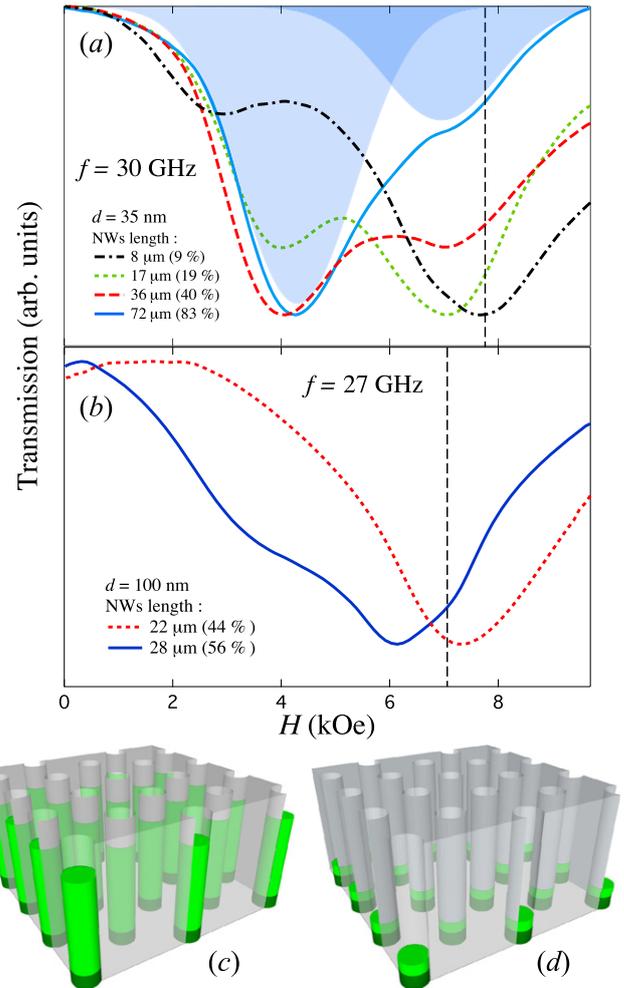


Figure 3. (a) FMR absorption spectra recorded at 30 GHz for arrays of Ni NWs with $d = 35 \text{ nm}$, $P = 12\%$ and lengths $h = 8 \mu\text{m}$, $17 \mu\text{m}$, $36 \mu\text{m}$ and $72 \mu\text{m}$. The shaded curves are gaussian distributions used in the two peak fit of the absorption spectra for the largest length NW array. (b) FMR spectra recorded at 27 GHz for two arrays of NWs with $d = 100 \text{ nm}$ and lengths of 22 and $28 \mu\text{m}$. The vertical dashed lines correspond to the resonance field $H_r^{[0]}$ given by equation (1), which is due only to the MS anisotropy contribution. Schematic representation of the two stages system for (c) long and (d) short NWs, where the poly- and single-crystalline stages correspond respectively to the dark and bright segments.

MS anisotropy contribution (vertical dashed-dotted line in figure 3(a)), further corroborates the presence of different ME anisotropy contributions associated to each crystalline segment along the NWs. Since the amplitude of an FMR absorption peak is proportional to the volume of probed magnetic material, longer (shorter) arrays of NWs are expected to display an increase (decrease) in the amplitude of the absorption peak corresponding to the single-crystalline segment in comparison with the amplitude of the absorption peak corresponding to the polycrystalline segment. Indeed, as shown in figure 3(a) the absorption spectra for the largest length NWs, as those of figure 3(c) displays a dominant absorption peak at lower resonance fields, whereas the opposite behavior is observed for the shorter NWs as those of figure 3(d). This observation corroborates the assumption that

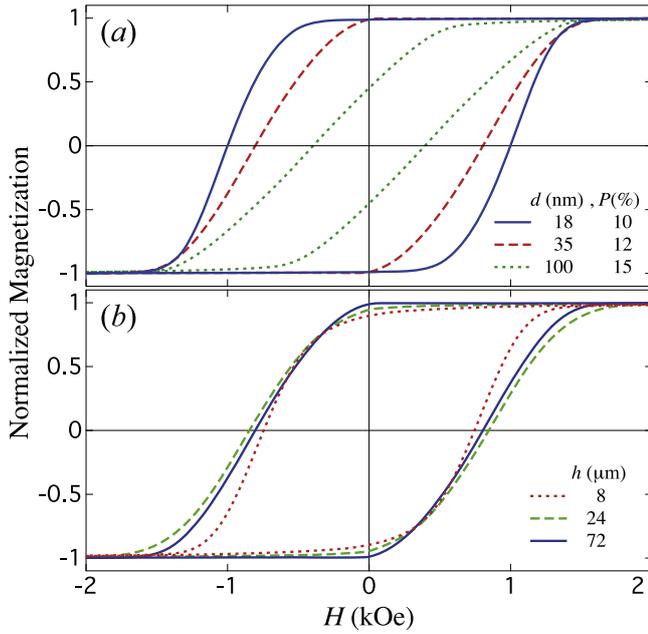


Figure 4. (a) Hysteresis loops recorded by applying the external field in the direction parallel to the NWs for arrays with (a) diameter and porosity equal to 18 nm and 10%; 35 nm and 12%; 100 nm and 15% and (b) $d = 35$ nm and $P = 12\%$ but with different length values of 8 μm , 24 μm and 72 μm .

the low and high field absorption peaks arise respectively from the second and the first crystalline segments of the NWs.

Furthermore, the hysteresis loops measured with the field applied along the NWs axes provide further evidence of the changes in their magnetic properties with both the NWs' diameter and length. As shown respectively in figures 4(a) and (b), the remanence squareness (M_r/M_s) increases as the diameter decreases and the length increases, indicating that depending which parameter is modified the uniaxial easy axis of magnetization is either weakened or reinforced along the axis of the NWs. The arrays of NWs of figure 4(a) correspond to those of figure 1(a), so the decrease of remanence and coercive field is clearly related to both, the different ME anisotropy contributions for each array and an increase of the dipolar interaction field between NWs for larger d and P , as suggested by the increase of the shearing of the hysteresis loops [33]. In the case of the arrays of NWs in figure 4(b) no significant effects due to shearing of the hysteresis loops are observed, indicating that the decrease of the remanence squareness as h is decreased is due to variations in the ME contribution for each array of NWs, as suggested by figure 3(a).

4. Discussion

Both FMR and magnetometry measurements show a significant increase of the effective magnetic anisotropy in these Ni NWs. Moreover, the fact that Py NWs behave as expected considering only shape anisotropy and dipolar interaction

effects, suggests a ME effect in Ni NWs as the origin of the high magnetic anisotropy. As mentioned before, the magnetocrystalline anisotropy in Ni is too low with respect to the MS contribution and to the observed increase in the effective anisotropy, so in the following it is neglected. However, the FMR spectra shown in figures 1(a) and 3(a), show a complex line-shape that suggest the presence of more than one absorption peak. In this sense, the FMR spectra are analyzed considering a two-stage growth. Since the amplitude of the absorption peaks are proportional to the probed volume, the absorption amplitude (T) for each peak, as those shown in figure 3(a), allows obtaining an approximate value of the length of both crystalline segments. In the present analysis, for each peak T is fitted to a two-peak Gaussian/Lorentzian function. For instance figure 3(a) shows the two gaussian distributions (shaded curves) used in the two-peak fit performed to the 72 μm long NW array. Since the total sample surface probed by the FMR experiment is the same for each sample, then T is proportional to the total length of the NWs, denoted by h . Let h_s and h_p be the lengths of the single- and poly-crystalline segments so that $h = h_s + h_p$, while T_s and T_p are their corresponding absorption amplitudes, then the ratio (r) between their lengths is

$$r = \frac{T_s}{T_p} = \frac{h_s}{h_p}. \quad (3)$$

Then, the length of the poly-crystalline segment can be expressed as a function of the total NW length and the ratio between the absorption amplitudes, which is determined from its two-peak Gaussian/Lorentzian fit, in particular

$$h_p = \frac{h}{1 + r}. \quad (4)$$

The total length of the NWs, h , has been determined from the cross section view of the sample using optical microscopy as shown in figure 5 (a) for a 50 μm thick AAO membrane and by SEM, as shown in figure 5(b) for a 90 μm thick AAO membrane. With this information and equation (4) it is then possible to determine h_p . Figure 5 (c) shows the comparison between the variations of h_p (filled circles) and h (empty circles) as a function of h for a series of samples with $d = 35$ nm. As observed, short NWs are mostly poly-crystalline ($h_p \approx h$) until h_p reaches a maximum value of about 12 μm , above which the length of the single-crystalline segment increases as h increases. Low enough NWs ($h \leq 12$ μm) have a small amount of [110] grains which give the low ME anisotropy contribution at lower resonance fields, in agreement with the FMR spectra in figure 3(a). Besides, as observed in figure 5(d), varying the diameter of the NWs for long enough arrays has a little effect on the length of the poly-crystalline stage. This figure shows an increase of h_p from 10.4 to 17.1 μm as d is increased from 18 to 100 nm (filled squares) for arrays of NWs with h in the range 28–40 μm (empty squares). The large length of these NWs insures that the obtained h_p values correspond to the maximum length of the poly-crystalline segment for each diameter, as suggested by figure 5(c) which shows that h_p tends to a limiting as h increases. The value $h_p = 17.1$ μm for

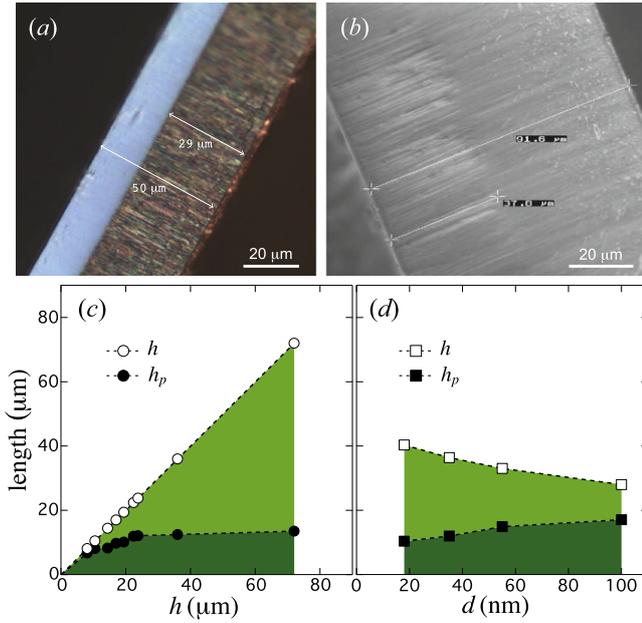


Figure 5. (a) Optical microscopy and (b) SEM micrographs of the cross section of two different AAO porous membranes, showing the length of the NWs and membrane thickness. Comparison between the total NWs length h (open symbols) and the length of the polycrystalline segment, h_p (filled symbols) as a function of: (c) the total length for NWs of constant diameter (35 nm) and (d) the NWs diameter. The dark and bright areas represent respectively the length of the poly- and single-crystalline segments of the NWs.

the 100 nm diameter array with $h = 28 \mu\text{m}$ means that $r < 1$, which explains why the main FMR absorption is located at high resonance fields corresponding to the polycrystalline stage absorption (see figure 1 (a)). Our results are then consistent with previous studies that already reported a two-stage growth mechanism in Ni NWs that can be controlled via the length of the NWs [31, 32]. As a consequence, h is a key parameter that allows to induce appreciable changes in the line-shape of the FMR absorption spectra for arrays of Ni NWs for whatever its diameter. Indeed, Dellis *et al.*, have shown that even large diameter ($d = 220 \text{ nm}$) and long enough Ni NWs are single crystalline with preferential orientation along the [110] direction parallel to the NWs [31]. Furthermore overall changes in the crystalline structure of the NWs are mediated by the variation of d [26–28], which in turn influence the value of h_p as observed in figure 5(d).

On the other hand, the analysis of the magnetic anisotropy of arrays of Ni NWs is discussed in terms of the ME energy which corresponds to an additional contribution that reinforces the easy axis of magnetization lying along the axis of the NWs. In the case of the FMR experiments each absorption peak in the spectra is associated to one of the two crystalline segments, where its corresponding resonance field $H_r^{[i]}$ is determined to a first approximation using the resonance condition

$$\frac{f_r}{\gamma} = H_r^{[i]} + H_{\text{ms}} + H_{\text{me}}^{[i]}, \quad (5)$$

where H_{ms} is the MS field given by equation (2), $i = p$ and $i = s$ stand respectively for the poly- and the single-crystalline segment and $H_{\text{me}}^{[i]} = 2 K_{\text{me}}^{[i]}/M_s$ is the uniaxial ME anisotropy field parallel to the axis of the NWs, being $K_{\text{me}}^{[i]}$ the ME energy associated to segment i . It must be stressed that the orientation of compressive or tensile stresses upon the NWs is unclear and needs further investigations, which is out of the scope of the present study. Therefore, the ME fields for each crystalline segment are considered as average fields that reinforce the easy anisotropy axis of the NWs. Equation (5) includes H_{ms} , which is the same for both single- and polycrystalline segments and since this field is known, equation (2), it follows that the ME field $H_{\text{me}}^{[i]}$ corresponds to the resonance field shift $\delta H_r = H_r^{[0]} - H_r^{[i]}$. As a consequence the ME anisotropy energy is given by

$$K_{\text{me}}^{[i]} = \frac{1}{2} M_s \delta H_r. \quad (6)$$

Complementary information about the ME contribution can be obtained from the uniaxial effective magnetic anisotropy energy $K_{\text{eff}}^{[A]}$ determined from magnetization curves. This energy is defined as the difference between the magnetic energies needed to saturate the sample from the demagnetized state, measured along the hard and easy directions of magnetization. Specifically, if m_{\perp} and m_{\parallel} are the normalized initial magnetization curves measured perpendicular and parallel to the axis of the NWs, then

$$K_{\text{eff}}^{[A]} = \frac{M_s}{2} \left[\int_0^{H_{s\perp}} m_{\perp} dH - \int_0^{H_{s\parallel}} m_{\parallel} dH \right], \quad (7)$$

where $H_{s\perp}$ and $H_{s\parallel}$ are the saturation fields in the corresponding applied field directions once m_{\perp} and m_{\parallel} reach the value 0.98. Figure 6 shows initial magnetization curves recorded by applying the external field in the directions parallel and perpendicular to the axis of an array of Ni NWs with $d = 35 \text{ nm}$ and $P = 12\%$. The integrals of equation (7) for each direction of the applied field are represented by the shaded areas beneath the curves. The value of $K_{\text{eff}}^{[A]}$ allows to obtain the ME energy $K_{\text{me}}^{[A]}$ from AGM experiments, which adds to the MS contribution $K_{\text{ms}} = (M_s/2)H_{\text{ms}}$, that is

$$K_{\text{me}}^{[A]} = K_{\text{eff}}^{[A]} - K_{\text{ms}}. \quad (8)$$

Magnetization curve measurements do not distinguish between the ME energy contributions of both crystalline segments, but they are incorporated into the ME energy given by equation (8). One may expect that, depending on the values of the diameter and length of the NWs, $K_{\text{me}}^{[A]}$ will be determined mainly in terms of $K_{\text{me}}^{[s]}$ or $K_{\text{me}}^{[p]}$.

Figure 7(a) shows the ME energies $K_{\text{me}}^{[s]}$ (circles), $K_{\text{me}}^{[p]}$ (squares) and $K_{\text{me}}^{[A]}$ (filled triangles) as a function of the diameter of the NWs, determined using equations (6) and (8). As expected, $K_{\text{me}}^{[s]}$ increases with reducing the diameter of the NWs in agreement with the increase of the single crystalline preferential growth at low diameters. Conversely, lower ME energy values are obtained from the polycrystalline segment of the NWs, where no clear dependence of $K_{\text{me}}^{[p]}$ with d is observed. The ME energy ($K_{\text{me}}^{[A]}$) obtained from initial

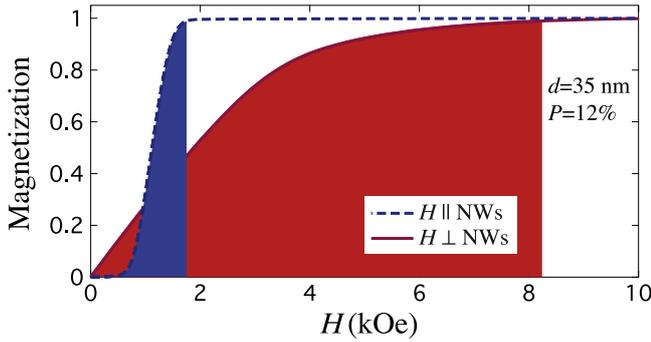


Figure 6. Initial magnetization curves recorded after AC demagnetization in the directions parallel (dashed line) and perpendicular (continuous line) to the NWs for an array with $d = 35$ nm and $P = 12\%$. Shaded areas correspond to the integrals in equation (7).

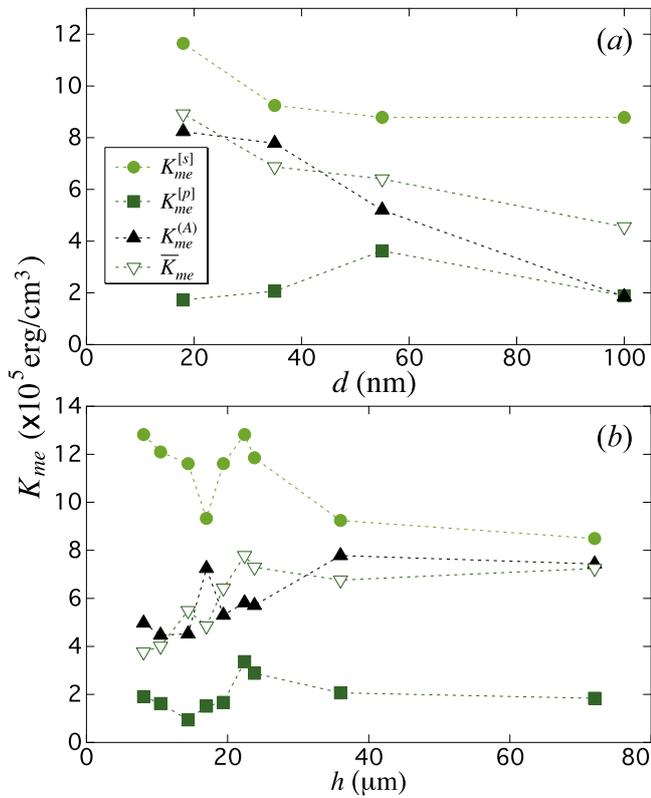


Figure 7. Variation of $K_{me}^{[s]}$, $K_{me}^{[p]}$ and $K_{me}^{[A]}$, obtained using equations (6) and (8), as a function of (a) the diameter and (b) the length of the NWs for arrays with $d = 35$ nm. The weighted average FMR ME energy (\bar{K}_{me}) determined using equation (9) is also displayed. Dotted lines are guides for the eye.

magnetization curves (filled triangles) decreases with increasing d and takes values in the whole range of about $1.9\text{--}8.2 \times 10^5 \text{ erg cm}^{-3}$. As seen in the figure, for low (large) diameter NWs, $K_{me}^{[A]}$ is very close to the characteristic values of the ME energy $K_{me}^{[s]}$ ($K_{me}^{[p]}$) determined from FMR experiments. This behavior is consistent with longer (shorter) polycrystalline segments as the NWs diameter increases (decreases), as observed in figure 5(d). The ME anisotropy measured from the hysteresis loops reflects the competition of these contributions which is weighted by the length of each

segment. Moreover, the intensity of the XRD peaks in the spectra shown in figures 2(a)–(c) are then mainly dominated by variations of r , which can be controlled by either varying the diameter or the length of the NWs.

Figure 7(b) shows the variation of $K_{me}^{[s]}$, $K_{me}^{[p]}$ and $K_{me}^{[A]}$ versus h in the range $8\text{--}72 \mu\text{m}$, for arrays of 35 nm diameter Ni NWs. As in figure 7(a), $K_{me}^{[p]}$ does not significantly change with h , which is in agreement with the results shown in figure 5(c), that show that h_p reaches a maximum value that does not depend on the total length of the NWs. Conversely, the strong variation of $K_{me}^{[s]}$ with either d or h shows that it is sensitive to volumetric variations, such that larger energies are present in low size single-crystalline segments. Besides the effective ME anisotropy, $K_{me}^{[A]}$ lies between $K_{me}^{[s]}$ and $K_{me}^{[p]}$ but it approaches to one of them whether the NWs are long or short enough. Since $K_{me}^{[A]}$ corresponds to an overall average ME energy, then it must result from the addition of both separate contributions, $K_{me}^{[s]}$ and $K_{me}^{[p]}$, weighted by their corresponding length ratios $r_p = h_p/h$ and $r_s = h_s/h = 1 - r_p$. The ME energy written as a volume weighted average reads

$$\bar{K}_{me} = r_p K_{me}^{[p]} + (1 - r_p) K_{me}^{[s]}, \quad (9)$$

whose variations with d or h (empty triangles), shown in figures 7(a) and (b), fairly explain the behavior of $K_{me}^{[A]}$. Consequently, equations (8) and (9) provide two different but equivalent methods for the determination of the overall average ME energy in Ni NWs.

The previous results show that a significant enhancement of the magnetic anisotropy is observed in either very long or low diameter Ni NWs embedded in AAO membranes. This unusual anisotropy enhancement is one order of magnitude higher than the magnetocrystalline anisotropy of Ni and is the result of an induced ME anisotropy contribution. As a consequence, effective (MS+ME) anisotropy energies as large as $1.4 \times 10^6 \text{ erg cm}^{-3}$ are obtained, so they are of the same order of magnitude and comparable to the MS anisotropy energy for arrays of Co NWs of about $4.3 \times 10^6 \text{ erg cm}^{-3}$. It must be stressed that this is the first time to our knowledge that this large effect is reported, which we attribute to the fact that most of the previous reports are focused on the study of the magnetic properties of short Ni NWs, with lengths in the range $6\text{--}12 \mu\text{m}$ [34–37]. Furthermore, our results are consistent with a two stage growth where the length of the initial polycrystalline segment decreases by decreasing the diameter of the NWs. Although the ME anisotropy of this segment is not significantly sensitive to size variations, the corresponding ME anisotropy of the single-crystalline segment does depends on both its diameter and length. So very high ME anisotropy values are obtained for NWs with very small single-crystalline segments which have very low lengths and low diameters. Besides, although the overall average anisotropy of the arrays corresponds to a weighted average of the ME anisotropies of both crystalline segments, it takes very high values for low diameter NWs with very short single-crystalline segments.

5. Conclusions

From AGM and FMR experiments we have shown the presence of a size-dependent ME anisotropy contribution, that is induced at room temperature in arrays of Ni NWs embedded into the pores of AAO membranes. Particularly, higher ME effects are observed in low diameter and very long NWs, leading to a ME anisotropy contribution that reinforces the easy axis of magnetization and exceeds the magnetostatic anisotropy of the NWs. Such an increase of the magnetic anisotropy, yields zero field resonance frequencies of up to four times the value due to the magnetostatic contribution and closer to characteristic values recorded for poly-crystalline Co NWs. Our results are consistent with a two stage crystal structure, where a short poly-crystalline segment at the beginning of the NWs growth is followed by a single-crystalline segment oriented along the [110] direction, parallel to the NWs axis. From FMR measurements different ME contributions are obtained for both crystalline segments, such that the contribution for the single crystalline segment is higher and size dependent. Measurements of initial magnetization curves along with a simple mathematical expression for the effective ME energy yield values that are consistent with an overall average ME energy, which can be obtained as a weighted average from the FMR ME contributions of the two crystalline segments. Understanding particular properties of nanocomposites like size and confinement effects on the magnetic properties of their constituents is of prime interest for the development of agile devices with tunable operation parameters.

Acknowledgments

This work was partly supported by CONACYT project CB-177896 and the 2015 UNAM-DGAPA-PAPIIT Program project IA102915. Y Velázquez-Galván acknowledges CONACYT for scholarship 348405. Financial support was partly provided by the Fédération Wallonie-Bruxelles (ARC 13/18-052 Supracryst).

References

- [1] Ross C A 2001 *Annu. Rev. Mater. Sci.* **31** 203
- [2] Richter H J 2007 *J. Phys. D: Appl. Phys.* **40** R149
- [3] Sharma M, Kuanr B K, Sharma M and Basu A 2014 *J. Appl. Phys.* **115** 17A518
- [4] Hamoir G, Piroux L and Huynen I 2013 *IEEE Trans. Magn.* **49** 4261–4
- [5] Hamoir G, De La Torre Medina J, Piroux L and Huynen I 2012 *IEEE Trans. Microw. Theory Tech.* **60** 2152–7
- [6] Kuanr B K, Veerakumar V, Marson R, Mishra S R, Camley R E and Celinski Z J 2009 *Appl. Phys. Lett.* **94** 202505
- [7] Darques M, De la Torre Medina J, Piroux L, Cagnon L and Huynen I 2010 *Nanotechnology* **12** 145208
- [8] Carreón González C E, De La Torre Medina J, Encinas A and Piroux L 2011 *Nano Lett.* **11** 2023–7
- [9] Biziere N, Mure E and Ansermet J P 2009 *Phys. Rev. B* **79** 012404
- [10] Abreu Araujo F, Piroux L, Antohe V A, Cros V and Gence L 2013 *Appl. Phys. Lett.* **102** 222402
- [11] Gopman D B, Bedau D, Mangin S, Fullerton E E, Katine J A and Kent A D 2014 *Phys. Rev. B* **89** 134427
- [12] Erokhin S and Berkov D 2014 *Phys. Rev. B* **89** 144421
- [13] Piroux L, Hamoir G, Lee M-G, Ferain E, Jonas A M, Huynen I and De La Torre Medina J 2011 *Appl. Phys. Express* **4** 115001
- [14] Eerenstein W, Mathur N D and Scott J F 2006 *Nature* **442** 759–65
- [15] Srinivasan G 2010 *Annu. Rev. Mater. Res.* **40** 153–78
- [16] Murthy D V B and Srinivasan G 2012 *Frontiers Phys.* **7** 418–23
- [17] Dubois S, Colin J, Duvail J L and Piroux L 2000 *Phys. Rev. B* **61** 14315–8
- [18] De La Torre Medina J, Darques M and Piroux L 2008 *J. Phys. D: Appl. Phys.* **41** 032008
- [19] Ghaddar A, Gieraltowski J, Gloaguen F, Zuberek R, Aleshkevych P, Kazmierczak J, Slawska-Waniewska A and Szymczak H 2009 *Acta Phys. Polon. A* **116** 1039–43
- [20] Piroux L, Hamoir G, Encinas A, De La Torre Medina J and Abreu Araujo F 2013 *J. Appl. Phys.* **114** 123907
- [21] Sousa C T, Leitao D C, Proenca M P, Ventura J, Pereira A M and Araujo J P 2014 *Appl. Phys. Rev.* **1** 031102
- [22] Encinas-Oropesa A, Demand M, Piroux L, Huynen I and Ebels U 2001 *Phys. Rev. B* **63** 104415
- [23] Sun L, Hao Y, Chien C-L and Searson P C 2005 *IBM J. Res. Dev.* **49** 79–102
- [24] Yin L F, Wei D H, Lei N, Zhou L H, Tian C S, Dong G S and Jin X F 2006 *Phys. Rev. Lett.* **97** 067203
- [25] Cullity B D and Graham C D 1972 *Introduction to Magnetic Materials* 2nd edn (New York: Wiley-IEEE) p 129
- [26] Wang X W, Fei G T, Xu X J, Jin Z and Zhang L D 2005 *J. Phys. Chem. B* **109** 24326
- [27] Wang X W, Fei G T, Chen L, Xu X J and Zhang L D 2007 *Electrochem. Solid State Lett.* **10** E1–3
- [28] Chu S-Z, Wada K, Inoue S and Todoroki S-I 2002 *Chem. Mater.* **14** 4595
- [29] Darques M, Encinas A, Vila L and Piroux L 2004 *J. Phys. D: Appl. Phys.* **37** 1411
- [30] Huang X H, Li G H, Sun G Z, Dou X C, Li L and Zheng L X 2010 *Nanoscale Res. Lett.* **5** 1057–62
- [31] Dellis S, Christoulaki A, Spiliopoulos N, Anastassopoulos D L and Vradis A A 2013 *J. Appl. Phys.* **114** 164308
- [32] Thongmee S 2008 Synthesis, structure and magnetic properties of nanowires and films by electrodeposition *PhD Thesis* M. Sc. Mahidol University, Thailand pp 105–8
- [33] Martínez Huerta J M, De La Torre Medina J, Piroux L and Encinas A 2012 *J. Appl. Phys.* **111** 083914
- [34] Nielsch K, Wehrspohn R B, Barthel J, Kirschner J, Fischer S F, Kronmüller H, Schweinböck T, Weiss D and Gösele U 2002 *J. Magn. Magn. Mater.* **249** 234–40
- [35] Ross C A *et al* 2002 *Phys. Rev. B* **65** 144417
- [36] Vega V, Prida V M, García G A and Vazquez M 2011 *Phys. Status Solidi a* **208** 553–8
- [37] Zhang J, Qin X, Torre B, Zeng H and Xu X-H 2014 *IEEE Trans. Magn.* **50** 1–4