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Characterization of ferromagnetic nanowires by partial first order reversal curves

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A nonparametric approach to the identification of magnetic anisotropies in ferromagnetic nanostructures is applied in order to study the influence of the bath acidity on the induced magnetic anisotropies in electrodeposited ferromagnetic nanowires. By using partial first order reversal curves (pFORC), we find a two-peak probability density function whose topology changes with the acidity of the electrodeposition bath. Numerical micromagnetic simulations suggest that this particular distribution originates in two populations of nonidentical nanowires with different magnetocrystalline anisotropies. Bath acidity values influence the balance between these two populations rather than the intrinsic properties of individual nanowires. © 2007 American Institute of Physics. [DOI: [10.1063/1.2778748](https://doi.org/10.1063/1.2778748)]

I. INTRODUCTION

Ferromagnetic nanostructures consist of assemblages of many ferromagnetic entities in which at least one dimension is less than 1 μm . These structures are interesting for the theoretical and experimental challenges they pose, and for their present and potential technological applications.¹ Since a major feature of ferromagnetism is hysteresis, many of the methods employed for the characterization of these materials are based upon their magnetization curves and consist of relating empirical parameters such as coercivity or remanence to intrinsic properties of individual magnetic entities, such as exchange energy constant, magnetic anisotropy, or saturation magnetization.

The small dimensions and the experimental difficulties related to the direct measurement of individual nanoparticles justify recent attempts to find new approaches for extracting information about individual magnetic entities from measurements of their assemblages.^{2–9} Among these, the first order reversal curve (FORC) diagrams^{10,11} have rapidly gained in popularity, due to the large amount of information which may be extracted from simple magnetization curves of the sample. However, the FORC measurement protocol can be very time consuming, especially when liquid He-based magnetometers are used. Moreover, such assemblages may present symmetry elements (points or axes) on their FORC diagrams¹² so that much of the measurement and computational time is spent in order to obtain redundant information about the sample. A faster approach that can exploit the eventual symmetry of FORC diagrams consists of measuring only a few points, adequately chosen on the reversal curves. For example, the switching field distributions may accurately be extracted from measurement points distributed in the vicinity of the Preisach plane diagonal.¹³ The distributions of these switching fields may supply valuable information about magnetic anisotropies in individual entities if accurate models for the magnetization reversal are employed.

In this article we use partial first order reversal curves in order to study the influence of the electrodeposition bath acidity on the magnetic anisotropies of CoFeP nanowires. The switching field distributions are evaluated at different levels of the bath acidity using a partial first order reversal curves (pFORC) approach and the topology of these distributions is then related to corresponding magnetocrystalline configurations by numerical micromagnetic simulations.

II. EXPERIMENTS AND SIMULATIONS

Nanowire arrays were obtained by dc electrodeposition of Co-Fe-P alloys into the pores of high-quality anodized aluminum oxide (AAO) templates.⁹ These arrays are characterized by narrow distributions of both nanowire diameters (45 nm) and interwire spacings (~ 100 nm) [Fig. 1(a)]. The growth of nanowires is uniform so that they may be considered to be of approximately the same length in each array [Fig. 1(b)]. We prepared four samples labeled A, B, C, and D which consist of arrays of CoFeP nanowires of approximately the same length but obtained at different pH values of the electrodeposition bath: 1.5, 2.2, 3.2, and 4.0. Energy dispersive X-ray (Oxford, Inca, Energy 300EDS) measurements were performed in order to study the composition of the electrodeposited alloy in these samples. We found a systematic decrease of the phosphorus content with increasing pH (Table I). Since this decrease is almost completely balanced by the increase in the amount of Fe, the Co content can be considered almost invariable for all four samples.

The distributions of switching fields in the direction parallel to the nanowire symmetry axes were obtained by 5-point first order reversal curve (pFORC-5) measurements¹³ using a Quantum Design Physical Property Measurement System (PPMS). The magnetic moment was measured to a precision of about 0.5% with a field resolution of $\Delta H = 5.6$ kA/m at applied fields ranging from -280 kA/m to $+280$ kA/m. Each sample was initially saturated in a strong magnetic field $H_{\text{sat}} = 280$ kA/m (point S in Fig. 2) and the field ramped down to the first reversal point, $O(H=0)$. The magnetic moment of the sample was then measured at three

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FIG. 1. SEM image of the AAO template (a) and side view of electrodeposited nanowires in sample D (b).

values of the applied magnetic field, 0, ΔH , and $2\Delta H$ after that the sample being again saturated. Further reversal fields H_{ri} were chosen to be negative multiples of ΔH , that is $H_{ri} \in \{-\Delta H, -2\Delta H, -3\Delta H, \dots, -i\Delta H, \dots, -H_{sat}\}$, so that the measurement of the i th partial reversal curve began by applying the field $H_{ri} = -i\Delta H$ (point R_i on Fig. 2). The magnetic moment m was then evaluated at five equidistant points centered at $H = +|H_{ri}|$ (point M_i), namely $|H_{ri}| - 2\Delta H, |H_{ri}| - \Delta H, |H_{ri}|, |H_{ri}| + \Delta H$ and $|H_{ri}| + 2\Delta H$, and the sample was again saturated, in preparation for the next reversal field $H_{r,i+1}$. After all partial first order reversal curves had been measured, the distribution S_{pFORC} of the switching fields H_c was obtained by evaluating the second order mixed derivative of m with respect to H and H_r (Ref. 13)

FIG. 2. Five-point first order reversal curves (pFORC-5) for sample B, obtained with a field resolution $\Delta H = 5.6$ kA/m.

$$S_{pFORC}(H_c) = - \frac{1}{2} \frac{\partial^2 m}{\partial H \partial H_r} \bigg|_{H=-H_r} \quad (1)$$

at all the median nodes M_i of each reversal curve. The switching fields in Eq. (1) are assumed to be identical to the critical fields $H_c = (H - H_r)/2$, as used in the Preisach formalism.¹⁴

The distributions $S_{pFORC}(H_c)$ obtained with the above algorithm for the four samples are shown in Fig. 3 (open circles). The topology of these distributions consists mainly of two peaks P_1 and P_2 whose positions and amplitudes change in a systematic manner with the value of the pH. A good fit of these distributions may be obtained with double-peak Gaussian functions (Fig. 3—full line). The bath acidity dependence of the positions of these two peaks is shown in Fig. 4. As the pH of the electrodeposition bath is increased, the peak P_1 shifts slightly to higher fields and diminishes in amplitude, whereas the secondary peak P_2 shifts rapidly to high fields, where it remains, while its amplitude increases constantly. Figure 4 suggests that pH may induce two types of modifications in the distribution of the switching fields: (a) shifts of the peaks along the critical field direction (modifications of the peak positions) or (b) variations of the populations corresponding to these two peaks (modifications of peaks in amplitude and width).

In order to explain the topology of the switching field distributions S_{pFORC} , we assume that the influence of the electrodeposition bath on the micromagnetic structure of ferromagnetic nanowires consists mainly of reorientations of Co magnetocrystalline c axes with changes in pH.¹⁵ Conse-

TABLE I. Physical and geometrical properties of the ferromagnetic arrays used in the pFORC analysis.

Sample	pH	Length (μm)	P (%)	Fe (%)	Co (%)
A	1.5	19.0	17.09	12.89	69.02
B	2.2	15.0	11.89	16.5	71.6
C	3.2	18.0	9.6	20.0	70.4
D	4.0	20.0	7.0	23.5	69.6

FIG. 3. Switching field distributions S_{pFORC} (points) and best fit with double-peak Gaussian functions (full line) for samples A (a), B (b), C (c), and D (d). The positions of the peaks are indicated by vertical dashed lines. The vertical thick lines on each graph correspond to the coercive field values of 9.9 kA/m and 198 kA/m as obtained by numerical micromagnetic simulations (Ref. 16) for individual Co nanowires with perpendicular and random MCA, respectively.

FIG. 4. Bath acidity dependence of the positions of the two peaks observed in the distribution of switching fields in electrodeposited CoFeP nanowires (open circles— P_1 and open triangles— P_2).

quently, we performed numerical micromagnetic simulations of individual Co nanowires characterized by three different orientations of the magnetocrystalline anisotropy axes (MCA) relative to the nanowire symmetry axis: perpendicular ($\theta_K=90^\circ$), parallel ($\theta_K=0^\circ$) and polycrystalline. A magnetocrystalline anisotropy constant of $k_u^{Co}=0.52 \times 10^6$ J/m³ has been considered for all these three configurations. In order to avoid the numerical problems that may arise when the applied field is exactly colinear with the easy axis,⁸ a slightly deviated MCA orientation ($\theta_K=0.5^\circ$) from the nanowire symmetry axis was considered instead of perfectly parallel MCA. The polycrystalline structure was modeled by discretizing the nanowires into small cubic cells of 4 nm edge and generating random values of θ_K inside the cells.¹⁶ The axial magnetization curves of single and isolated nanowires whose geometry is similar to those of the samples were simulated in applied magnetic fields between -280 kA/m and $+280$ kA/m with a field step of about 5 kA/m. The calculated coercive field values, corresponding to the magnetization reversal of these three configurations are $H_{c\perp}=9.9$ kA/m, $H_{c\parallel}=630$ kA/m, and $H_{c,rand}=198$ kA/m for

perpendicular, parallel, and random orientations of these axes, respectively. $H_{c\perp}$ and $H_{c,\text{rnd}}$ values are indicated by vertical thick lines on each subfigure of Fig. 3. Both peaks are located between these two limits or slightly above, as indicated in Fig. 4.

Comparison between the experimental and numerical results suggests that the magnetic entities responsible for the experimental distributions in Fig. 3 are nanowires characterized by either perpendicular or random orientations of MCA with respect to the nanowire symmetry axis (uniform configurations of parallel MCA cannot be important since $H_{c\parallel} \gg H_{\text{sat}}$). This assumption, as well as its implications for the homogeneity and structure of electrodeposited nanowire arrays are discussed in the following section.

III. DISCUSSION

The fact that bath acidity influences the orientation of MCA in Co-based electrodeposited nanowires has been demonstrated by measurements of ferromagnetic resonance (FMR) spectra¹⁵ and in-plane (IP) magnetization processes.⁹ The general idea which emerges from these studies is that at small values of the bath acidity pH the magnetocrystalline c -axes are preponderantly perpendicular to the nanowires' symmetry axes and become almost parallel to these axes at higher values of the pH. From this, it might be supposed that the MCA in nanowires might be controlled by simply adjusting the acidity of the electrodeposition bath. Although this picture may be correct when averaged properties of the array are under discussion, we shall consider the possibility that the double-peak distributions in Fig. 3 reveals that, inside the array, nanowires may present different properties with respect to each other.

It is important that the Co content is almost the same for all samples (Table I) so that any variation in MCA strength arises primarily from changes in c -axis orientations. The contribution of Fe to the total anisotropy field is small as its MCA strength (k_u^{Fe}) is much smaller than the geometric (shape) anisotropy (k_g^{Fe}) of the nanowires ($k_g^{\text{Fe}}/k_u^{\text{Fe}}=37.7$ whereas for cobalt $k_g^{\text{Co}}/k_u^{\text{Co}}=2.36$). Since the axial coercive field is roughly proportional to the total axial anisotropy field,¹⁷⁻¹⁹ the main contributions to the switching fields in individual nanowires are the geometric (shape) anisotropy of Co ($k_g^{\text{Co}}=1.23 \times 10^6$ J/m³), the geometric anisotropy of Fe ($k_g^{\text{Fe}}=1.81 \times 10^6$ J/m³), and the magnetocrystalline anisotropy of Co ($k_u^{\text{Co}}=0.52 \times 10^6$ J/m³). The first two contributions are invariant with respect to the orientation of MCA and hardly change with the alloy composition ($k_g^{\text{Fe}} \approx k_g^{\text{Co}}$) so that, in such a ferromagnetic nanowire with strong shape anisotropy, we may assume that the coercive field is well approximated by

$$H_c \propto (p_{\text{Fe}}k_g^{\text{Fe}} + p_{\text{Co}}k_g^{\text{Co}} + k_u) \approx k_g^{\text{Co}} + k_u, \quad (2)$$

where p_{Fe} and p_{Co} are the fractions of Fe and Co in the alloy respectively, and k_u is the equivalent (averaged) MCA constant of the nanowire ($k_u=k_u^{\text{Co}}$ only for nanowires with uniform distributions of MCA). If a particular value $H_{c,\text{rnd}}$ for completely random orientations of MCA is known, we may easily find the proportionality constant in Eq. (2) and conse-

TABLE II. Positions of peaks and ε_K values for a reference value $H_{c,\text{rnd}}$ of 198 kA/m. σ_1 and σ_2 are the variances of the Gaussian functions used to fit the peaks P_1 and P_2 , respectively.

Sample	$\varepsilon_{K1} \pm \sigma_1 / H_{c,\text{rnd}}$	$\varepsilon_{K2} \pm \sigma_2 / H_{c,\text{rnd}}$
A	0.187 ± 0.08	0.33 ± 0.30
B	0.351 ± 0.18	0.94 ± 0.08
C	0.372 ± 0.10	1.06 ± 0.18
D	0.377 ± 0.12	0.87 ± 0.22

quently, the coercive field H_c for a particular value of k_u

$$H_c = \frac{H_{c,\text{rnd}}}{k_g^{\text{Co}}} (k_g^{\text{Co}} + k_u) = H_{c,\text{rnd}} \varepsilon_K, \quad (3)$$

where $\varepsilon_K = (k_g^{\text{Co}} + k_u) / k_g^{\text{Co}}$. The parameter ε_K may be used in order to evaluate the MCA strength (k_u) in individual nanowires if an estimate of the coercive field $H_{c,\text{rnd}}$ is available. Amorphous (or polycrystalline) nanowires are characterized by $k_u=0$ and consequently nearly unitary values of ε_K . Any increase of ε_K above 1 may indicate parallel orientations of MCA with respect to the nanowire symmetry axis whereas ε_K should decrease below 1 when MCA are preponderantly perpendicular to the nanowire axis. The values of this parameter as well as the variances for the two peaks in three are given in Table II.

Since the values of ε_{K1} for the first peak are very small, we may assume that this peak corresponds to nanowires with MCA oriented preponderantly perpendicular to the nanowires' symmetry axes. This assumption is confirmed by micromagnetic simulations, as the value of $H_{c\perp}$ is very close to the lowest limit for the location of the peak P_1 [Fig. 3(a)]. The fact that this limit is reached by very few nanowires, that is $S_{\text{pFORC}}(H_{c\perp})$ is very small [Fig. 3(a)], means that there are very few nanowires whose MCA are perfectly perpendicular to the nanowire axis. Apart from sample A, the secondary peak P_2 is characterized by ε_K values very close to unity (Table II) that is the nanowires corresponding to this peak do not have any preferential orientation of MCA and may be considered as polycrystalline.

At small pH values, nanowires with perpendicular c axis (peak P_1) appear to be favorite, parallel orientations of these axes (P_2) being strongly inhibited [the amplitude of P_2 in Figs. 3(a) and 3(b) is much smaller than the amplitude of P_1]. Moreover, as S_{pFORC} presents a relatively sharp distribution of switching fields [peak P_1 in Fig. 3(a)], the nanowires appear to be almost identical, with a switching (coercive) field of about 30 A/m. Increasing values of pH favor the growth of nanowires with more c -axes oriented parallel to the symmetry axis, and consequently characterized by much larger values of the switching (coercive) field. The effect of this increase of pH values is twofold. On one hand, it increases the MCA strength in nanowires of small coercive field (shifting the peak P_1 toward larger critical fields), and on the other hand, it leads to the appearance of a second type of nanowires, with larger coercive fields (peak P_2).

The slight shift of the peaks with increasing values of the pH is very important when the tailoring of MCA in individual nanowires is envisaged. The coexistence of the two

peaks at certain values of the pH demonstrates that the electrodeposition process may induce strong nonuniformities in the distribution of MCA in individual nanowires and consequently different magnetic properties of the nanowires with respect to each other. It seems that increased values of pH influence the probability of having nanowires of larger MCA rather than uniformly increase the MCA in all nanowires of the array. Moreover, certain values of the MCA strength in individual nanowires may simply be impossible to obtain by varying the pH, as the gap between the two peaks can be very important. For example, as we may see in Fig. 3, none of the four samples could provide nanowires with coercive fields of about 125 kA/m.

IV. CONCLUSION

The pFORC strategy employed in this study is appropriate for characterizing magnetic nanostructures. Essential information concerning intrinsic properties of magnetic entities, such as magnetocrystalline anisotropy field and MCA orientations, may be extracted from the distributions of switching fields. Electrodeposited CoFeP nanowire arrays present strong non-uniformities at certain values of the bath acidity. These nonuniformities lead to the appearance of multi-peak distributions of the switching fields on the pFORC diagram. The main switching fields corresponding to these peaks may be related to intrinsic magnetic anisotropies in ferromagnetic nanowires by numerical micromagnetic simulations. In CoFeP electrodeposited nanowires, these peaks may appear to correspond to populations of nanowires with varying crystal structures and magnetic properties.¹⁵ However, in the present study we found that intrinsic properties of these nanowires cannot be fully controlled by the pH of the electrodeposition bath, since important gaps between populations of nanowires with different magnetic properties may be observed despite large variations of bath

acidity. This may be a major problem when wire arrays are fabricated for various applications. For example, if individual wires are to be used as nanocarriers for magnetic manipulation in microfluidic devices, both their homogeneity and uniformity are important issues. The pFORC measurements described here can provide accurate information about the strength and distribution of MCA.

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