

## Exchange bias in Co/CoO core-shell nanowires: Role of antiferromagnetic superparamagnetic fluctuations

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The magnetic properties of Co ( $\langle D \rangle = 15$  nm,  $\langle L \rangle = 130$  nm) nanowires are reported. In oxidized wires, we measure large exchange-bias fields of the order of 0.1 T below  $T \sim 100$  K. The onset of the exchange bias, between the ferromagnetic core and the antiferromagnetic (AFM) CoO shell, is accompanied by a coercivity drop of 0.2 T which leads to a minimum in coercivity at  $\sim 100$  K. Magnetization relaxation measurements show a temperature dependence of the magnetic viscosity  $S$  which is consistent with a volume distribution of the CoO grains at the surface. We propose that the superparamagnetic fluctuations of the antiferromagnetic CoO shell play a key role in the flipping of the nanowire magnetization and explain the coercivity drop. This is supported by micromagnetic simulations. This behavior is specific to the geometry of a one-dimensional system which possesses a large shape anisotropy and was not previously observed in zero-dimensional (spheres) or two-dimensional (thin films) systems which have a high degree of symmetry and low coercivities. This study underlines the importance of the AFM superparamagnetic fluctuations in the exchange-bias mechanism.

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### I. INTRODUCTION

Magnetic nanowires are of prime interest both scientifically and for applications in the nanotechnology industry (in magnetic memories,<sup>1</sup> magnetic recording media,<sup>2</sup> sensors,<sup>3</sup> or microwave devices<sup>4</sup>). The magnetic properties of nanowires are essentially governed by the very strong shape anisotropy giving rise to high coercive fields which may have applications for permanent magnets fabrication.<sup>5</sup> Exchange-biased (EB) systems such as ferromagnetic (FM)/antiferromagnetic (AFM) layers or core/shell FM/AFM spherical particles are characterized by the Néel temperature  $T_N$ , corresponding to the ordering of the antiferromagnetic layer, and the blocking temperature  $T_{EB}$  corresponding to the apparition of the exchange-bias field  $H_{EB}$ , usually lower than  $T_N$ .<sup>6–10</sup> Most of the recent studies of the exchange-bias mechanism have been performed on thin-film systems<sup>7–9,11</sup> since they permit a good control of the thickness and textures and the temperature dependence of the exchange field  $H_{EB}$  has been extensively studied.<sup>8,12</sup> On the other hand, the temperature dependence of the coercivity is studied although it can exhibit a variety of behaviors depending on the anisotropy of the AFM layer.<sup>8</sup> Actually, it can be difficult to study the temperature dependence of the coercivity due to the microstructured character of the material.<sup>8</sup> However, it has been shown that, in the case of exchange-biased systems whose AFM layer exhibits a small anisotropy, a coercivity peak can arise around the blocking temperature.<sup>8</sup> In this paper, we

discuss the exchange-bias properties of Co nanowires with large coercive fields, mainly due to the one-dimensional (1D) geometry,<sup>5</sup> and show that this 1D character leads to a specific exchange-bias behavior, in connection with the superparamagnetic relaxation of the CoO grains present at the surface of the nanowires. The paper is organized as follows: in Sec. II, we present the magnetic nanowires. Section III gives the experimental results obtained from magnetometry measurements. The experimental results are discussed in Sec. IV. Micromagnetic simulations are presented in Sec. V.

### II. MAGNETIC NANOWIRES

Co nanowires<sup>13</sup> have been synthesized by reduction in liquid polyol.<sup>14,15</sup> Transmission electron microscopy (TEM) shows Co nanowires with a mean diameter  $\langle D \rangle$  of 15 nm and a mean length  $\langle L \rangle$  of 130 nm (see Fig. 1). The standard deviation on the diameter distribution  $\sigma_d$  is small ( $\sim 10\%$ ). The length distribution is broader with a standard deviation  $\sigma_L \sim 20\%$ . The nanowires are well preserved from oxidation as long as they remain in their polyol solution. In order to perform magnetic characterizations, the nanowires are collected by centrifugation and washed several times with ethanol. In this case, the wires oxidize at their surface.<sup>14,15</sup> After a few weeks the system reaches a stable magnetic state via a passivation mechanism.<sup>16,17</sup>

High-resolution TEM (HRTEM) and x-ray diffraction show very well-crystallized wires in the metallic hcp phase

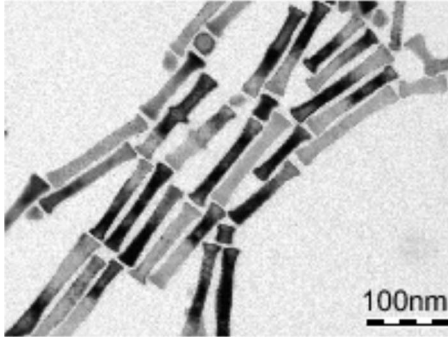


FIG. 1. TEM image of Co nanowires (Ref. 13).

with the crystallographic *c* axis parallel to the wires axis (see Fig. 2). The HRTEM image presented on Fig. 2 shows a wire with a mean diameter of 13 nm that consists of a core of metallic cobalt coated by a thin oxide layer of CoO. The diffraction pattern calculated from the image of the Co core was indexed as the  $[1\bar{1}20]$  zone axis of the hcp structure showing that the *c* axis is parallel to the wire axis. The core is nearly single crystal, only few stacking faults diffuse lines are observed perpendicular to the  $[0002]$  direction. The CoO oxide layer is continuous all over the wire edges. Its thickness inferred from HRTEM images is estimated to  $1.2 \pm 0.1$  nm on the edge of the wires and to  $1.4 \pm 0.1$  nm on the tips. Diffraction patterns calculated on the edge and on the tip of the wire are indexed as the  $[\bar{1}10]$  zone axis of the fcc structure with two distances of 0.212 nm and four distances of 0.245 nm corresponding, respectively, to the (002) and (111) reflections of the  $Fm\bar{3}m$  cubic cobalt oxide CoO.<sup>18</sup> The crystallographic orientation relationships between the native oxide and the metal are:  $\text{CoO}[\bar{1}10](111) \parallel \text{Co}[1\bar{1}20](0001)$  and  $\text{CoO}[\bar{1}10](110) \parallel \text{Co}[1\bar{1}20](1\bar{1}00)$  on the tip and the edges, respectively. These relationships allow to (i) minimize the mismatch between cobalt oxide and cobalt parameters on the edges: 0.212 and 0.202 nm for the (200) oxide and (0002)

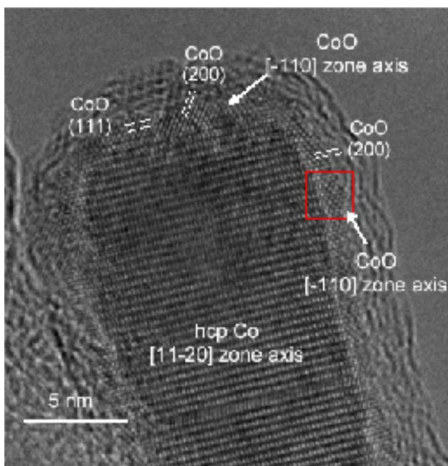


FIG. 2. (Color online) HRTEM image of the tip of a Co wire showing the local structure of the Co wire surrounded by a CoO shell (1.2 nm thickness).

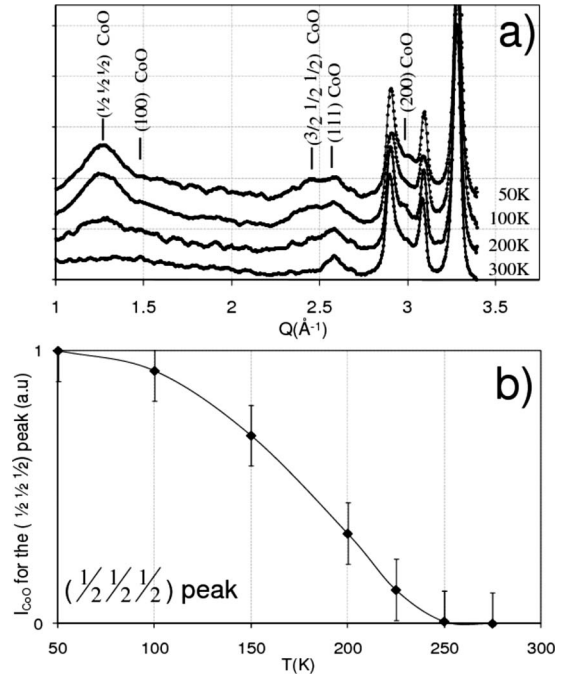


FIG. 3. (a) Neutron-diffraction pattern for oxidized Co nanowires for temperatures between 50 and 300 K. The CoO peaks are indexed following the cubic-lattice diffraction pattern. The three nonindexed peaks above  $Q=2.89 \text{ \AA}^{-1}$  correspond to the Co structural diffraction peaks (Ref. 13). (b) Intensity of the  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  CoO diffraction peak as a function of the temperature. The CoO shell orders antiferromagnetically between 220 and 250 K.

cobalt distances, respectively, and (ii) retain the hexagonal symmetry of the hcp Co (0001) plane in the CoO (111) plane on the tip. The oxide layer appears monocrystalline both on the tip and on the edges but is globally polycrystalline because of the different orientations on the wire facets. Therefore, from the bulk measurement point of view, the CoO layer will be considered as disordered and composed of crystallites of various sizes.

The roughness of the interface between the Co core and the oxide layer is smaller than 0.5 nm showing that we have very well-defined interfaces, which have a quality equivalent to thin films deposited by vacuum techniques. Bulk CoO is an AFM with a Néel temperature  $T_N=293$  K. It has been shown that CoO layers as thin as 1 nm on oxidized Co particles still present AFM order close to room temperature<sup>17,19</sup> and that the Néel temperature in very thin epitaxial CoO layers can even be increased well above room temperature.<sup>10</sup> In the case of Co/CoO nanospheres, a  $T_N$  of about 235 K was reported.<sup>20</sup>

We performed neutron powder-diffraction experiments on the G4.1 spectrometer at the Laboratoire Léon Brillouin in order to determine  $T_N$  [see Fig. 3(a)]. Above  $T_N$ , bulk CoO has the rocksalt structure<sup>21</sup> whereas below  $T_N$  there is a small trigonal and tetragonal distortion.<sup>20,22,23</sup> Thus bulk CoO crystal structure becomes monoclinic ( $C2/m$  phase) when the antiferromagnetic order sets in. However we indexed the peaks following the cubic lattice diffraction pattern in a first approximation as it is usually done. At room temperature we observe the two nuclear peaks (111) and (200) at, respec-

tively, 2.54 and 2.94  $\text{\AA}^{-1}$ . When the temperature is lowered, three magnetic peaks appear: the  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  and  $(\frac{3}{2}\frac{1}{2}\frac{1}{2})$  peaks at, respectively,  $q_{2,a}=1.27 \text{\AA}^{-1}$  and  $q_{2,b}=2.43 \text{\AA}^{-1}$  from the AFM-II order and the (100) peak at  $q_1=1.47 \text{\AA}^{-1}$  from the AFM-I order. The temperature dependence of the AFM-II peaks intensity [see Fig. 3(b)] shows that the AFM order sets in around 230 K. This is comparable to what has been observed in Co/CoO spherical particles.<sup>20</sup> The (100) peak of the AFM-I order is barely visible. However Gaussian fits of the pattern suggest that the (100) peak appears only below 150 K, contrary to what was observed in Ref. 20. Also note that above 250 K, a very broad magnetic diffuse scattering is observed around the  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  position suggesting that AF correlations already exist at higher temperatures. From the present data, we consider that the Néel temperature of the CoO shell around the wires is around  $T_N=230$  K, which is lower than the bulk value. Using the Scherrer formula, the width of the  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  peak corresponds to a magnetic correlation length of 1–2 nm. This is in agreement with the thickness of the oxide shell. Note that neutron diffraction measures an instantaneous picture of the AF ordering of the CoO shell so that it is not sensitive to superparamagnetic fluctuations (slower than  $10^{-14}$  s) of the small CoO crystallites. The measured  $T_N$  temperature thus does not correspond to the blocking temperature of the CoO crystallites.

### III. EXPERIMENT

The nanowire powders were characterized by superconducting quantum interference device (SQUID) magnetometry. We considered two types of samples: (i) nonoxidized Co wires, which were used as reference samples and kept in their butane-diol synthesis solution<sup>24</sup> and (ii) Co dried powders exposed to air, which led to a natural oxidation. Figure 4 presents the evolutions of the exchange-bias field  $H_{EB}$  and coercive field  $H_C$  for these systems as a function of temperature. In these measurements, the samples were field cooled under 5 T and the hysteresis cycles were measured while increasing the temperature from 5 to 300 K. The hysteresis cycles have been obtained by applying external magnetic fields ranging from  $-5$  T to  $+5$  T. The hysteresis loops are not perfectly square and the magnetization at remanence is around  $0.7M_s$  for nonoxidized wires and around  $0.6M_s$  for oxidized wires. Two typical hysteresis cycles are presented in Fig. 4(a).

In the case of nonoxidized samples [triangles in Fig. 4(b)], no exchange bias is observed and the coercive field decreases monotonously from  $\mu_0 H_C \sim 0.9$  T at low temperatures to 0.5 T at room temperature. In the case of oxidized samples (circles), an exchange-bias field  $H_{EB}$  appears below  $T_{EB} \approx 100$  K. This exchange-bias field reaches 0.1 T at low temperatures. The most striking feature is that the coercive field  $H_C$  dependence is not monotonous since the coercive field decreases down to a *minimum* at  $T_{EB}$ , then reaches a maximum at about 200 K, and finally decreases again when reaching room temperature. It thus appears that  $\mu_0 H_C$  is maximum (0.6 T) at  $T \approx T_N \approx 200$  K. Similar results (not shown here) were obtained on three different batches of samples.

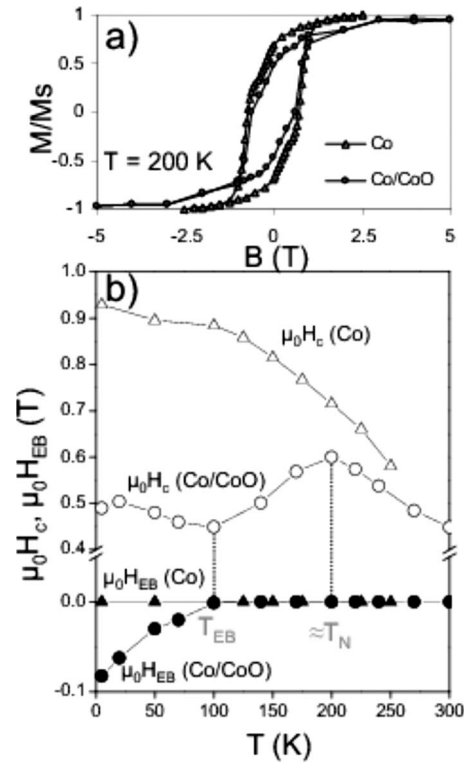


FIG. 4. (a) Typical hysteresis cycles obtained from the Co and Co/CoO nanowires. (b) Temperature dependence of the coercive field  $\mu_0 H_C$  (open symbols) and the exchange-bias field  $\mu_0 H_{EB}$  (filled symbols) for nonoxidized Co (triangles) and oxidized Co (circles) nanowires. The samples were cooled under  $B=5$  T and the measurements were performed with an increasing temperature. The lines are guide for the eyes.

Below  $T_{EB}$ , the increase in  $H_C$  with decreasing temperature, along with the increase in  $H_{EB}$ , is in qualitative agreement with previous studies.<sup>7,8,25–28</sup> However, the fact that the coercivity goes up upon warming between  $T_{EB}$  and  $T_N$  is unexpected. As we shall argue, this is due to the presence of superparamagnetic fluctuations of the AFM CoO grains. For elongated systems, the main contributions to the coercivity of the system arise from the shape anisotropy  $K_{sh}$  of the wires which is almost temperature independent and from the Co uniaxial magnetocrystalline anisotropy  $K_{mc}$  which decreases from  $8 \times 10^5 \text{ J/m}^3$  at 5 K down to zero at 500 K.<sup>29</sup> Thus a monotonous variation in the coercive field would be expected. We argue that our measurements unambiguously show that the temperature behavior of the coercive field is related to the EB phenomenon. The comparison of the measurements on nonoxidized and oxidized Co wires [see Fig. 4(b)] shows that the oxidation, and thus the EB mechanism, leads to a drop of the coercivity of about 0.2 T at the blocking temperature.

To our knowledge, all reports on the Co/CoO system in the literature show that the coercive field monotonously increases below  $T_{EB}$ .<sup>25,26</sup> In a few reports, on some other exchange-bias systems, a maximum of the coercive field around the onset of the blocking temperature  $T_{EB}$  is observed (Ref. 8 and references therein, Refs. 30 and 31). We should point out that these observations have been made on very



low coercivity systems where  $H_C$  increase is only of a few mT and is attributed to the increase in the AFM anisotropy around  $T_{EB}$ . In the present case the effect is in the *opposite direction* since we observe a *coercivity* minimum at  $T_{EB}$ . As evidenced by the temperature dependence of  $H_C$ , the AFM surface layer modifies the core FM magnetization up to almost  $T_N$ , which is well above the onset of a static exchange bias at  $T_{EB}$ . Magnetization relaxation measurements have thus been carried out to assert whether the observed exchange-bias effects are concomitant with a slowing down of the superparamagnetic fluctuations of the AFM grains at the nanowire surface.

The magnetization relaxation was measured using SQUID (in a permanent mode with 15 s extraction time) at small positive fields (3 mT) after saturation under 5 T [see Fig. 5(a)]. The time decay of the magnetization was first fitted using a phenomenological stretched exponential expression:  $M(t) = M_c + M_0 \exp(-t/\tau)^\beta$ , where  $M_c$  is the magnetization at infinitely long times (static part),  $M_0$  is the magnetic moment of the fluctuating volume,  $\tau$  is the relaxation time, and  $\beta = 0.4$  is a stretch factor, indicative of a distribution of relaxation times in the sample, giving the best agreement with the experimental data. For single-size particles, we would have  $\beta = 1$ . The fact that  $\beta$  is far off unity is strongly indicative of a broad size distribution. For monodispersed superparamagnetic objects with uniaxial anisotropy  $K$ , the temperature dependence of the relaxation time  $\tau$  is related to the energy barrier  $\Delta E$  separating the two stable states through the Arrhenius expression:  $\tau = \tau_0 \exp(\Delta E/k_B T)$ , where the energy barrier is driven by the total anisotropy energy  $K$  and the volume  $V$  of the particles:  $\Delta E = KV$ . We define  $T_N = 200$  K, the temperature at which the coercive field is maximum. As shown in Fig. 5(b), the relaxation time  $\tau$  is first very short above  $T_N$  and then increases quickly upon decreasing temperature down to 50 K where it finally levels off down to the lowest temperature. The behavior of the relaxation time, characterized by a progressive slowing down of the relaxation, and the broad temperature range between  $T_N$  and  $T_{EB}$  suggests that the CoO layer is composed of a collection of anisotropic AFM grains with a broad size distribution which will relax with a characteristic time controlled by their respective energy barriers  $\Delta E$ .

In the case of a wide (almost flat) distribution of particle size and anisotropy barriers, the behavior of the magnetization can be described by the relation:<sup>32</sup>  $M(t) = M_0 - S(T) \ln(t - t_0)$ , where  $S(T)$  is the magnetic viscosity. This dependence is well followed in the time range  $t > 100$  s [see Fig. 5(a)]. The viscosity parameter is presented on Fig. 5(c). At low temperatures, the viscosity  $S(T)$  is low because most of grains are blocked and thus only a very small fraction of the sample can relax. Upon, warming we observe a round maximum at 80 K and then a steady decrease at higher temperatures. The broad size distribution of the AFM grains means that, at a given temperature, larger grains will tend to order along the FM magnetization while smaller grains remain superparamagnetic. At low temperatures, only the smallest grains will be superparamagnetic while the larger ones are locked into one of their stable magnetization configuration; hence a longer relaxation time in average and a smaller viscosity. At high temperatures, the global viscosity of the sys-

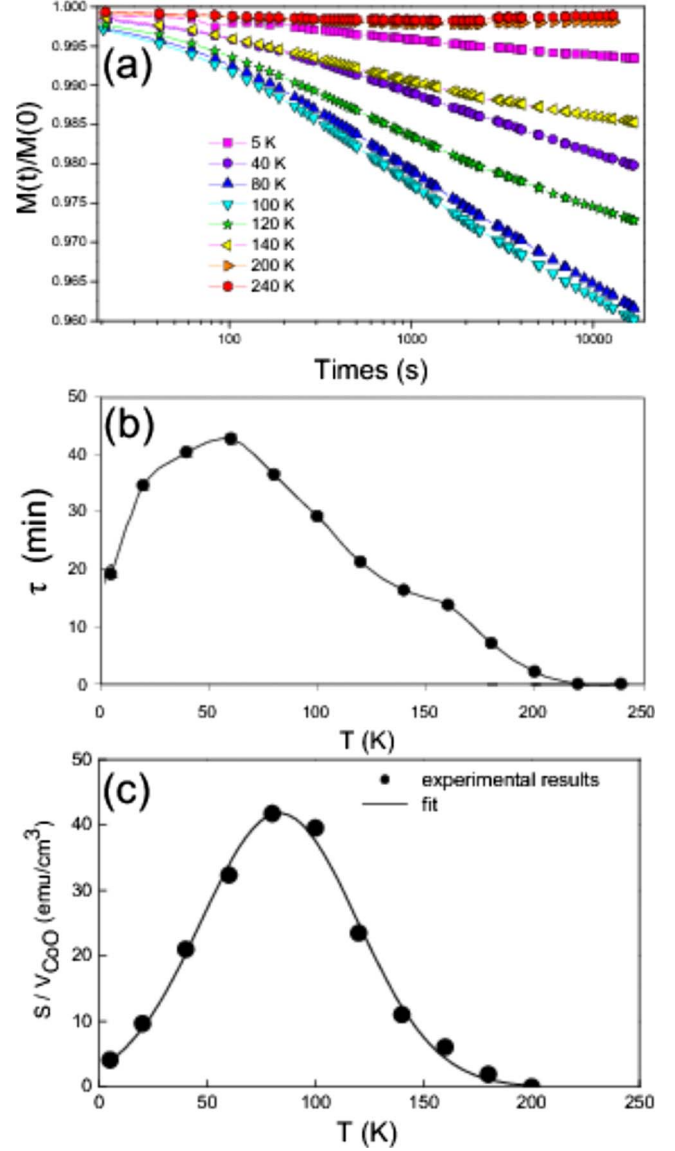


FIG. 5. (Color online) (a)  $M(t)/M(t=0)$  as a function of time for Co/CoO nanowires under 3 mT after saturation at 5 T. (b) Temperature dependence of the magnetization relaxation time for oxidized Co/CoO nanowires extracted from the expression  $M(t) = M_c + M_0 \exp(-t/\tau)^\beta$  with  $\beta = 0.4$  kept fixed throughout. (c) Magnetic viscosity  $S(T)$ , as a function of the temperature, extracted from the expression  $M(t) = M_0 - S(T) \ln(t - t_0)$ .

tem decreases due to the fact only the few remaining large grains are contributing to the relaxation.<sup>33</sup>

The viscosity  $S(T)$  is usually related to the distribution of energy barriers through  $S(T) = k_B T M_S / \Delta E_{m,T}$ , where  $M_S$  is the spontaneous magnetization of the CoO layer and  $\Delta E_{m,T}$  is the mean energy barrier of the remaining grains that still relax at a temperature  $T$ .<sup>34–36</sup> Larger grains, with higher energy barrier, are blocked while smaller grains relax more rapidly than the time window of the measurement. The quantity  $\Delta E_{m,T}$  is equivalent to the inverse of a distribution function  $f(\Delta E_m)$  [with  $\int_0^\infty f(\Delta E_m) d\Delta E_m = 1$ ] whose form can be either a flat distribution [ $f(\Delta E_m) = 1/W$  between two extrema separated by  $W$ ] or a Gaussian-type distribution around a

mean activated energy  $k_B T^*$ :  $f(\Delta E_m) = A \exp\{-k_B(T^* - T)/W\}^2$  with  $A = (1/\sqrt{\pi W})(T^*/T)$ . The best agreement is found for the latter model with  $T^* = 83 \pm 1$  K and a width  $W = 35 \pm 2$  K as shown in Fig. 5(c). From the absolute values of the viscosity  $S(T)$ , normalized by the volume fraction of CoO present in the nanowire (assuming a 1.5 nm shell thickness), we find that the spontaneous magnetization of the CoO shell is  $M_S = 15.2 \pm 0.1$  emu/cm<sup>3</sup>, a value much lower than the theoretical value (224 emu/cm<sup>3</sup>). It implies that the volume fraction which is “active” represents only 7% of the total volume of CoO in the materials. A similar result trend was found in the case of granular CoO layers<sup>37</sup> or powders.<sup>38</sup> Equating the obtained mean activated energies  $k_B T^*$  for both compounds with the usual expression for the energy barrier ( $\Delta E = KV$ ) and assuming that the uniaxial anisotropy is  $K = 5 \times 10^5$  J/m<sup>3</sup> (Refs. 17 and 39) leads to active volumes of the CoO grains which are in the range of 1.6–2.4 nm<sup>3</sup>.

To summarize, below  $T_N$ , the AFM moment fluctuations of the CoO freeze progressively as the temperature is decreased;<sup>40</sup> leading to a low-temperature rise of the relaxation time and a maximum of viscosity below  $T_{EB}$ . Interestingly, we note that the static part of the magnetization,  $M_C$ , is temperature dependent with a sharp decrease below 60 K. This could be explained by the pinning of the FM moments from the metallic core in contact with the AFM grains. The physical origin of the superparamagnetism could be attributed to a small fraction (7% as found from the experiment) of uncompensated spins at the FM/AFM interface.<sup>20,41–44</sup>

#### IV. DISCUSSION

The previous measurements give the following insight into the way the exchange-bias mechanism sets in our nanowires system. We have unambiguously shown that the blocking temperature where the exchange bias appears ( $T_{EB} \approx 100$  K) is well below the ordering temperature of the AFM CoO shell ( $T_N \sim 220$  K). This can be accounted for by the fact that the CoO shell is composed of small grains which are subject to strong superparamagnetic fluctuations down to rather low temperatures.

We propose the following description of the magnetic properties of our systems as a function of the temperature (see Fig. 6). Above the Néel temperature the coercivity of the wires increases with decreasing temperatures because of the increase in the magnetocrystalline anisotropy of the Co. Below the Néel temperature  $T_N$ , a magnetic coupling takes place between the CoO grains and the Co core of the wires, even though all the CoO grains are still in a superparamagnetic state. In all reported systems such as spherical particles or thin films, this leads to an increase in the coercivity by creating new loss mechanisms. On the contrary, in our nanowires, we observe a significant drop of the coercivity, by up to 0.25 T, when the temperature is decreased. The detailed mechanism of this coercivity drop is discussed in the next section. The coercivity drop is larger with decreasing temperature because: (i) the AFM moment increases when the temperature decreases [see Fig. 3(b)], (ii) the AFM superparamagnetic fluctuations slow down [see Fig. 5(b)] which enhances the AFM-FM coupling. Eventually, at a tempera-

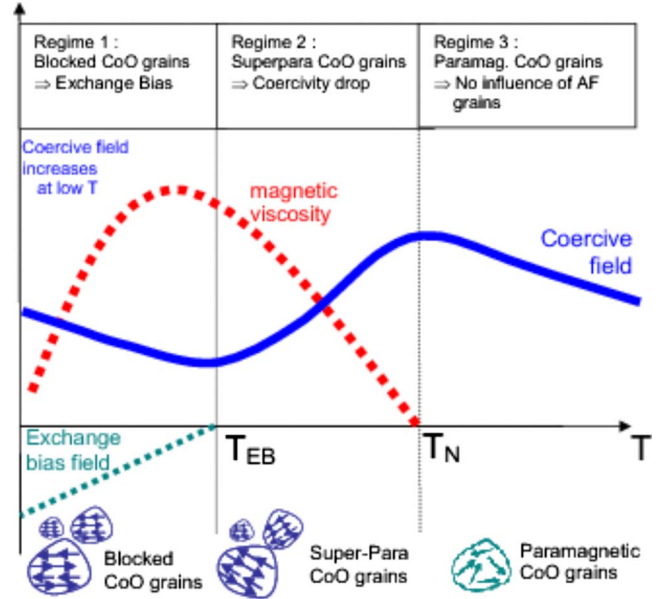


FIG. 6. (Color online) Scenario of the magnetization and relaxation processes in oxidized nanowires. We distinguish three regimes: (1) below the blocking temperature  $T < T_{EB}$ , the CoO particles are blocked and a finite exchange-bias field appears; (2) between the blocking temperature and the Néel temperature  $T_{EB} < T < T_N$ , the CoO particles are antiferromagnetically ordered but are subject to superparamagnetic fluctuations; (3) above the Néel temperature  $T_N$ , the CoO shell is not magnetically ordered and there is no effective interaction between the FM wire core and the AFM shell.

ture  $T_{EB}$ , the largest CoO particles are blocked and this gives rise to a finite exchange-bias field  $H_{EB}$ . Below the temperature  $T_{EB}$ , more and more CoO particles get blocked so that the exchange-bias field increases when the temperature is further decreased. Note that the blocked CoO particles do not contribute anymore to the drop of coercive field but only to the exchange field. Thus below  $T_{EB}$ , the coercivity follows the same slope as the nonoxidized wires [see Fig. 4(b)].

The interaction between the AFM shell and the FM core directly reflects in the magnetic viscosity temperature dependence. The magnetic viscosity appears as soon as  $T_N$  is reached. As the temperature is decreased, and the AFM fluctuations slow down, the viscosity increases. Eventually, below  $T_{EB}$ , as more and more CoO particles get blocked they do not contribute anymore to the viscosity. At very low temperatures where all the CoO particles are blocked, the viscosity becomes very small.

We underline that this scenario is very different from the usual observations in exchange-bias systems. Experimental reports together with modeling<sup>30,45</sup> show that when the temperature is decreased, the coercive field  $H_c$  increases to reach a maximum at  $T_{EB}$  and then  $H_c$  decreases again when the temperature is further decreased. In our system, because of the specific 1D geometry, a minimum of coercivity is observed at  $T_{EB}$ . This is discussed in the following section.

#### V. MODELING

As described above, the magnetic behavior of the nanowires is strongly influenced by the oxide shell surrounding

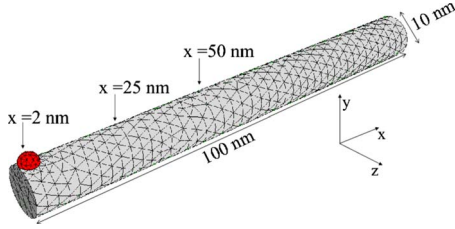


FIG. 7. (Color online) Typical mesh used for the micromagnetic calculations in presence of one hemisphere placed at the edge of the wire.

them. In order to qualitatively understand the role of the interactions between a magnetic Co wire and its CoO shell, we performed simulations with the NMAG micromagnetic modeling package.<sup>46</sup> The studied model object is a 100-nm-long, 10-nm-diameter cylindrical wire which is representative of the experimental objects. The magnetic parameters used correspond to typical values for hcp cobalt epitaxial thin films,<sup>47</sup> saturation magnetization  $M_S=1400 \text{ kA m}^{-1}$ , and exchange constant  $A=1.2 \times 10^{-11} \text{ J/m}$ . The magnetocrystalline anisotropy is neglected. The distance between two nodes of the mesh was taken four times smaller than the exchange length  $\ell_{ex}=\sqrt{2A/\mu_0 M_S^2} \approx 9.8 \text{ nm}$  (see Fig. 7).

As stated above, the key ingredients are the nanometer size CoO particles which compose the shell around the wire. For the simulations, we consider three different regimes: (i) below the blocking temperature  $T < T_{EB}$ , the CoO particles are blocked and a finite exchange-bias field appears; (ii) between the blocking temperature and the Néel temperature  $T_{EB} < T < T_N$ , the CoO particles are antiferromagnetically ordered but are subject to superparamagnetic fluctuations; and (iii) above  $T_N$ , the CoO shell is not magnetically ordered and there is no effective interaction between the wire core and the shell.

In the high-temperature regime  $T > T_N$ , the simulation is straightforward and leads to a coercive field of 471 mT when the field is aligned along the wire axis. Of course, in the case of randomly aligned wires with respect to the field, the coercive field due to the shape anisotropy is reduced by a few tens of mT due to the misalignment of the field with the wires. When the temperature is decreased from room temperature to  $\sim 200 \text{ K}$ , the coercive field increases as expected from the magnetocrystalline anisotropy linear temperature dependence of Co between 200 and 300 K (Ref. 29) ( $K_{mc} \approx 5 \times 10^5 \text{ J/m}^3$  at 300 K and  $\approx 6.5 \times 10^5 \text{ J/m}^3$  at 200 K).

In the low-temperature regime,  $T < T_{EB}$ , we consider that the wire is coated with small particles, whose magnetic moments are blocked along the  $x$  direction. These particles are modeled as half hemispheres (see Fig. 7) and correspond to the blocked CoO particles. When the temperature decreases the number of blocked AF particles increases. Thus, in the simulations, we considered a wire coated with an increasing number of such small blocked particles with a diameter of 4 nm (see Fig. 8 inset). Figure 8 presents the evolution of the exchange-bias field  $H_{EB}$  as a function of the total biased surface  $S$  around the wire. The total surface of the wire is  $3100 \text{ nm}^2$ . One can observe that a few pinning points which represent only a small fraction of the wire surface (7%) are

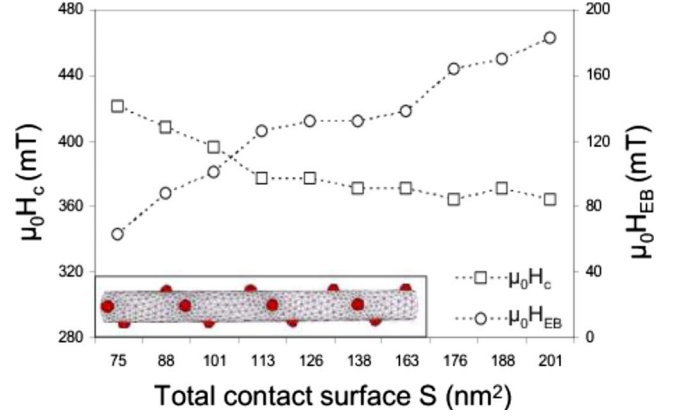


FIG. 8. (Color online)  $\mu_0 H_{EB}$  and  $\mu_0 H_C$  measured on the hysteresis cycle calculated along the wire axis in presence of more and more blocked particles around the wire.  $S$  is the total surface in contact between the blocked particles and the wire. The particles are homogeneously placed along the wire as shown in the inset.

sufficient to induce large exchange-bias fields ( $\sim 0.2 \text{ T}$ ), which are of the same order of magnitude as what is experimentally observed. Note however, that the exchange at the interface was taken as  $A_{FM-AFM}=1.2 \times 10^{-11} \text{ J/m}$  which overestimates the efficiency of the exchange-bias field. Note also that the emergence of blocked grains barely affects the coercive field. The coercive field is reduced from 470 mT without bias to 370 mT with 7% of biased surface. This qualitatively explains why at low temperatures, when most of the AF grains are blocked, the coercive field is not fully recovered in the oxidized wires compared to the nonoxidized wires [see Fig. 4(b)]. It suggests that the CoO grains act as nucleation points which promote the reversal of the wires and reduce the coercivity.

In the intermediate regime,  $T_{EB} < T < T_N$ , the situation is more complex. The relaxation measurements have shown that the CoO grains in the shell have a broad size distribution range so that there is also a broad distribution of the AFM fluctuation frequencies. It is presently impossible or at least very difficult to tackle numerically such a complex problem in the dynamic regime. Nevertheless, in this intermediate regime, we think that it is possible to give some insight of the role of fluctuating magnetic grains at the surface of the wires provided some approximations are made. The first point to note is that the characteristic reversal time of a 100 nm Co wire is of 4 ns, as obtained from dynamic micromagnetic simulations using a damping constant  $\alpha=0.02$ .

In the theory of superparamagnetism, the relaxation time  $\tau$  is related to the energy barrier  $\Delta E$  separating two stable states of a magnetic particle through the Arrhenius expression:  $\tau=\tau_0 \exp(\Delta E/k_B T)$ . The energy barrier is essentially driven by the uniaxial anisotropy energy  $K$  and the volume  $V$  of the particles:  $\Delta E=KV$ . The relaxation constant  $\tau_0$  is on the order of  $10^{-9} \text{ s}$ . If we thus consider fluctuations of the AFM grains and use an anisotropy constant  $K=5 \times 10^5 \text{ J/m}^3$ ,<sup>17,39</sup> the characteristic reversal time of 4 ns corresponds to a volume of the AFM particles of the order of  $10 \text{ nm}^3$ . Smaller particles will fluctuate much faster than the reversal time of the wire and their interaction with the wire is likely to aver-



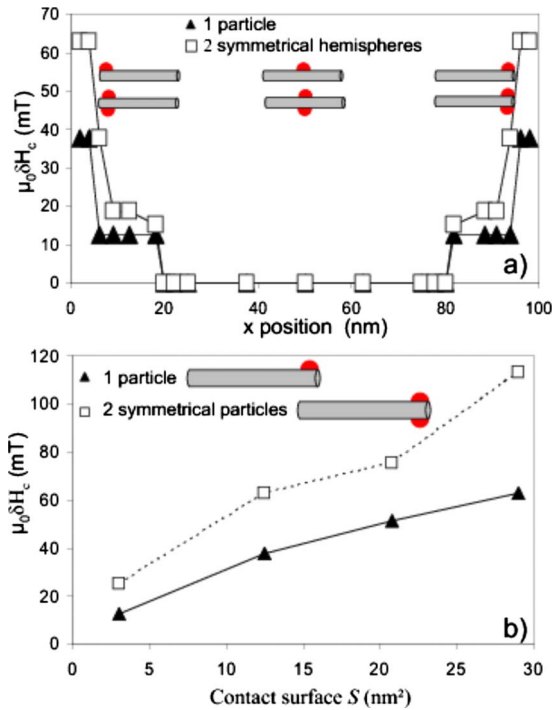


FIG. 9. (Color online) (a) Drop of the coercivity [ $\delta H_c = H_c(\text{isolated wire}) - H_c(\text{wire} + \text{particles})$ ] in presence of one (triangles) or two (squares) symmetrical hemispheres of 2 nm radius at different positions along the lateral surface of the wire. (b) Drop of the coercivity ( $\delta H_c$ ) in presence of one (squares) or two particles (triangles) of different sizes at the tip of the wire.  $\delta H_c$  is proportional to the surface in contact between the particles and the wire. Lines are guide for the eyes.

age out to zero. Bigger particles will fluctuate much slower and can be considered as static during the wire reversal. We thus make the assumption that the very small CoO grains will not play a key role in this intermediate regime while the bigger particles will behave as static objects with respect to the wire reversal so that static micromagnetic calculations may provide realistic account of the interactions between the Co wire and the CoO grains. The second assumption we are making is that the CoO grains behave mostly as nucleation points for the magnetic reversal of the wires. In order to model the CoO grains as nucleation points, we modeled them as small ferromagnetic grains with their magnetization free to rotate coupled to the Co wire with an exchange constant  $A = 1.2 \times 10^{-11}$  J/m. The CoO grains are thus represented as semihemispheres around the Co wire (see Fig. 7).

We first assessed the role of the position of these nucleation points along the Co wire [see Fig. 9(a)]. The calculation was performed with hemispheres of volume 17 nm<sup>3</sup> (2 nm radius), the surface  $S$  in contact with the ferromagnetic wire thus being 12.5 nm<sup>2</sup>. We find that the addition of such an hemisphere at the surface of the wire can induce a significant drop  $\delta H_c$  in the coercive field ( $\sim 40$  mT) when it is placed close to the wire tip [ $\delta H_c$  represents the difference of coercive field between the value obtained from the isolated wire (471 mT) and the value obtained from the wire surrounded by particles]. On the other hand, such nucleation points placed in the middle of the wire do not induce any

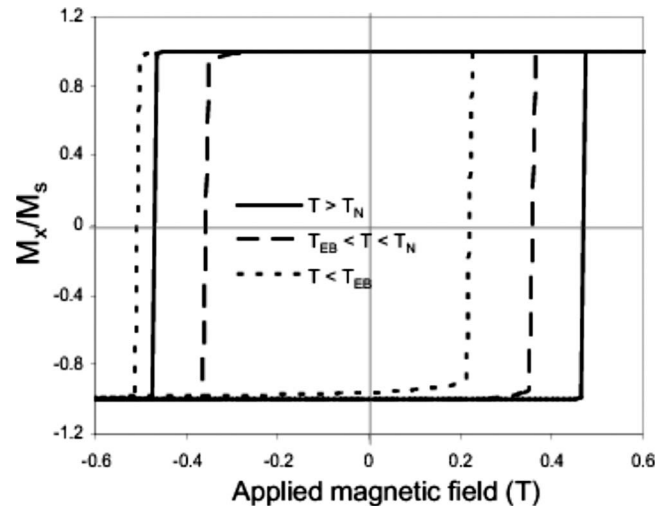


FIG. 10. Typical hysteresis cycles calculated in the three temperature regimes. Solid line:  $\mu_0 H_c = 471$  mT, long dashed line:  $\mu_0 H_c = 360$  mT, short dashed line:  $\mu_0 H_c = 365$  mT and  $\mu_0 H_{EB} = 145$  mT.

drop in the coercive field. The coercive drop can be almost doubled to ( $\sim 70$  mT) by simply putting a second symmetrical nucleation point. The sensitivity to the nucleation point position can be explained by the distribution of the demagnetizing field which is localized near the tips of the wire and is close to zero in the rest of the wire.<sup>48</sup> In the presence of a hemisphere located close to the tips of the wire, the demagnetizing field interacts with the nucleation point. This promotes an easier magnetization reversal and thus a smaller coercive field. It is thus likely that it is mostly the CoO particles located near the tips of the wires which are responsible for the coercivity drop observed in our systems.

We also investigated the effect of the nucleation point volume or contact surface. Nucleation points of increasing contact surfaces with the Co wire were considered (from 3 to 28 nm<sup>2</sup>). Figure 9(b) represents the drop in coercivity as a function of the contact surface. It varies quasilinearly from 12 to 60 mT for surfaces  $S$  varying from 3 to 30 nm<sup>2</sup>. The coercivity drop can be doubled if two particles are placed symmetrically at the end of the wire. These calculated drops are of the same order of magnitude as the ones experimentally observed. In the same way as before, large grains placed far from the wires tips do not have any influence on the coercive field. Contrary to the case of AFM grains at the surface of a thin film, where an increase in the coercive field is usually observed near the blocking temperature,<sup>49,50</sup> we observe a drop of coercivity in our nanowires when the AFM grains interact with the wire. This is due to the 1D geometry which is very sensitive to the AFM grains which behave as nucleation points promoting a magnetization reversal contrary to the case of thin films, where AFM grains usually behave as pinning centers which drag the magnetization.

Figure 10 presents three typical hysteresis in the three different temperature regimes for a magnetic field applied along the wire. The solid-line cycle corresponds to an isolated wire having no interaction with the CoO particles ( $\mu_0 H_c \approx 471$  mT). The long dash cycle corresponds to a wire

coated with nucleation points (2 nm radius hemispheres) covering 7% of the wire surface. The coercive field is reduced to 360 mT. The short dash cycle corresponds to a wire coated with pinning points (2 nm radius hemispheres) covering 7% of the wire surface. The coercive field is still reduced to 360 mT and a finite exchange-bias field appears  $\mu_0 H_{EB} \approx 145$  mT.

## VI. CONCLUSION

We have presented a study of the exchange-bias phenomenon in Co/CoO nanowires. We have shown that the AF ordering temperature of CoO oxidation shell is rather high ( $T_N \sim 230$  K). The exchange-bias field reaches values on the order of 0.2 T at low temperatures. We show that a minimum of coercivity is observed around the blocking temperature  $T_{EB} \sim 100$  K which is unambiguously related to the exchange-bias mechanism. Magnetization relaxation measurements show that this effect finds its origin in the superparamagnetic fluctuations of the oxidized AFM CoO layer. This proves that the exchange-bias mechanism sets in well above  $T_{EB}$ . Such a dramatic effect on the coercivity properties was not observed in previous studies because zero-

dimensional systems (spheres) (Refs. 17, 19, and 26) and two-dimensional systems (thin films) (Refs. 8, 10, 45, 51, and 52) have a high degree of symmetry and low coercivities. On the other hand, in the 1D geometry of nanowires the coercivity is dominated by shape anisotropy effects. We suggest that the large drop of coercivity is due to blocked AFM particles which act as nucleation points and promote the magnetization reversal of the wires. This conclusion is supported by micromagnetic simulations in which we can qualitatively reproduce several of the features of the experimental measurements. This study underlines the importance of the AFM superparamagnetic fluctuations in the exchange-bias mechanism.

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