Field-dependent energy barriers in Co/CoO core-shell nanoparticles

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We perform atomistic modeling of Co/CoO nanoparticles with a diameter of a few nanometers and realistic values of the exchange and anisotropy parameters in order to study the field-dependent energy barriers under forward and backward reversal of the magnetization. The barriers are extracted from the constrained energy minimization using the integration of the Landau-Lifshitz-Gilbert equations and the Lagrange multiplier method. We show that the applied field and the interface exchange strength have opposite effects on the values of the energy barriers. In particular, while the backward (forward) energy barrier increases (decreases) linearly with the strength of the interface exchange coupling, it decreases (increases) almost quadratically with the applied magnetic field. Our results are in good agreement with the well-known Meiklejohn-Bean model of exchange bias, and allow us to analyze the limits of applicability of the macrospin approach to the study of energy barriers in core-shell Co/CoO nanoparticles.

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I. INTRODUCTION

The exchange bias phenomenon was first reported nearly sixty years ago [1]; however a complete understanding of it is still lacking. Many research articles appear every year aiming to clarify the physical properties that accompany this phenomenon and its underlying mechanism in thin films and nanoparticles [2]. From the technological point of view, exchange bias is used in magnetic recording information technology, for example, to pin the magnetization of the pinned layer in magnetic recording heads. The thermal stability of a bit of information is of critical importance, since bits are becoming smaller and recoding media thinner [3]. In 2003 Skumryiev *et al.* [4] suggested that it is possible to increase the thermal stability of recording media, i.e., to "beat the superparamagnetic limit," through the use of the exchange bias phenomenon. They have shown that Co nanoparticles with a diameter of about 4 nm embedded in a paramagnetic matrix become superparamagnetic at 10 K while for nanoparticles in an antiferromagnetic (AF) matrix this happens at 290 K. Later Evans *et al.* [5] showed numerically that indeed coupling to an antiferromagnetic material in core-shell magnetic nanoparticles increases the magnetization energy barrier, but unfortunately, at the same time the energy barrier for the backward reversal of the opposite to the current magnetization state decreases. Alternatively, they have proposed the use of core-shell nanoparticles with exchange bias for heat-assisted magnetic recording in the situation when the core and shell are strongly coupled and at the remanence only one reversal barrier exists. These examples show that the evaluation of energy barriers in core-shell nanoparticles with exchange bias have fundamental and applied interest.

In a series of previous works on modeling of the magnetic hysteretic behavior of core-shell nanoparticles, including the archetype system Co/CoO (see, e.g., Ref. [6]), AF and ferromagnetic (FM) exchange coupling constants of the order of the anisotropy energy ($J \approx k_{AF}$) have been used. Assuming a reasonable CoO anisotropy value ($k \sim 10^{-15}$ ergs/atom), as in the present work, such a low value of the exchange coupling in the nanoparticle shell corresponds to extremely low Néel temperature of CoO ($T_N \sim 20$ K), similarly to the case of Ref. [6]. In order to observe exchange bias in such a situation, an anisotropy value in the shell, of the order of the exchange parameter, is required to quench the spin directions even for low temperatures. In some cases this may be reasonable since some measurements of T_C and T_N for Co and CoO nanoparticles (as for example in Refs. [4,7]) show values smaller than in the bulk, although maybe not so much.

At the same time, for Co/CoO core-shell nanoparticles it is also common to observe values of T_C and T_N similar to the bulk values [7]. In particular, for magnetic recording applications one should aim at the synthesis of nanoparticles with high T_C and T_N. In this situation the anisotropy in the shell cannot be of the order of the exchange parameter but more reasonably should be a small fraction of it, as assumed by Evans *et al.* [5,8]. These authors also showed that in this situation a stable exchange bias phenomenon occurs in the region where the interface coupling is approximately equal to or below 1% of the bulk Co exchange.

In the present work, we evaluate numerically the coercive field, the exchange bias field, and the energy barriers in core-shell Co/CoO nanoparticles following an atomistic approach and using values of Co/CoO parameters close to the bulk ones [5,8]. Our results indicate that in this realistic situation, the magnetic behavior of the core-shell nanoparticle is reasonably well described by a simplified macrospin model [1]. Comparing the results of the atomistic and the mesoscopic model we are able to define the limits of validity of the latter. The importance of our findings lies in the fact that the mesoscopic model can be used to relate directly the energy barriers, which are microscopic physical quantities not directly measured experimentally, to the experimentally measured exchange bias field. We underline that this link between the microscopic (barriers) and macroscopic (exchange bias field) quantities does not require knowledge of the interfacial exchange constant, which cannot be easily extracted from experiments. Furthermore, our results establish a quadratic scaling of the energy barriers in Co/CoO core-shell nanoparticles with the applied field, which is an issue of practical interest in magnetic recording applications.

In Sec. II we describe the atomistic model for Co/CoO core-shell nanoparticles considered in the present article, and in Secs. II A and II B we present the numerical results of the hysteresis loops and energy barriers using this atomistic model, respectively. In Sec. III we propose a simple mesoscopic theoretical model for Co/CoO core-shell nanoparticles and we compare its predictions with the atomistic results. Section IV concludes the article.

II. ATOMISTIC MODEL

We consider Co/CoO core-shell magnetic nanoparticles of spherical shape which are cut off from a simple cubic lattice. We study two different nanoparticle sizes, the first one with a core diameter of $L = 9$ atomic sites ($N_{\text{core}} = 365$) and the second one with a core diameter of 11 atomic sites ($N_{\text{core}} = 691$). In both cases, a shell which is two atomic sites thick ($N_{\text{shell}} = 656$ and $N_{\text{shell}} = 956$, respectively) is assumed. Taking the lattice constant equal to $a = 0.25$ nm, the chosen sizes correspond to total diameters of $d = 3.0$ nm and 3.5 nm, respectively. The system size was altered slightly in order to achieve a different arrangement of the shell spins and check the robustness of our conclusions against this change. The magnetic structure of the nanoparticle is modeled by a Heisenberg Hamiltonian with uniaxial anisotropy. Under application of an external field, the Hamiltonian is given by

$$\mathcal{H} = -\sum_{i,j} J_{ij}\boldsymbol{s}_i \cdot \boldsymbol{s}_j - \sum_i k_i s_{i,z}^2 - \sum_i \mu_i \boldsymbol{H} \cdot \boldsymbol{s}_i, \quad (1)$$

where $\boldsymbol{s}_i$ is the unitary vector of the atomic magnetic moment, μ_i is the atomic magnetic moment, k_i is the on-site uniaxial anisotropy constant, and J_{ij} is the exchange constant between moments i and j, which is assumed nonzero between nearest neighbors only. The direction of anisotropy is assumed parallel to the z axis in both materials. In our simulations we have used the values $J_{FM} = 11.2 \times 10^{-14}$ ergs ($T_C = 1390$ K), $J_{AF} = -4.2 \times 10^{-14}$ ergs ($T_N = 400$ K), $k_{FM} = 4.644 \times 10^{-17}$ ergs/atom, $k_{AF} = 50k_{FM}$, and $\mu_{FM} = \mu_{AF} = 1.5\mu_B$, where {FM,AF} = {core,shell}. The values of these parameters are very close to bulk values of Co and CoO, and noticeably the anisotropy energy is three orders of magnitude smaller than the exchange energy $k_{FM(AF)} \ll J_{FM(AF)}$. The interfacial exchange J_{int} is an unknown parameter and is expressed as a fraction of the core exchange (J_{FM}).

A. Hysteresis loops

The hysteresis loops are obtained by integration of the Landau-Lifshitz-Gilbert (LLG) equations for each atomic spin [5,8]. A dominant mechanism leading to exchange bias is the formation of a net moment at the AF interface due to the uncompensated spins. Experimentally, this state, which is called the field-cooled state (FC), is achieved by cooling down the system in an external magnetic field through the Néel temperature, leading to the FC state, characterized by a net AF moment. In principle, the same state of the two-phase system could be achieved under application of a high field that saturates both phases. While this approach is hard to achieve in the laboratory, it is computationally feasible and faster to simulate than the true FC process. In our simulations we get

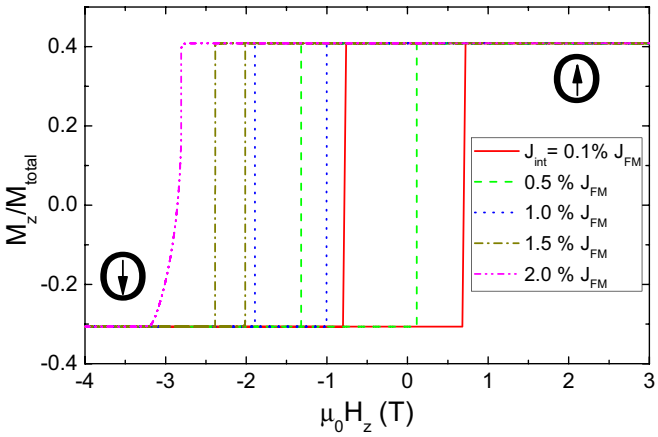

FIG. 1. Hysteresis loops for various strengths of the interfacial coupling for the 3 nm nanoparticle. M_z is the z component of the nanoparticle magnetization and M_{total} is the magnitude of the magnetization when all magnetic moments (core and shell) point in the same direction.

the FC state applying a very high magnetic field ($\mu_0 H_{\max} = 10$ T, where μ_0 is the permeability of free space), which settles the interfacial spins initially in the upward direction and creates noncompensated spins at the interface. The total energy is minimized after that at smaller field values leading to the hysteresis loop. The results of the hysteresis loop with an applied field along the easy axis, $\boldsymbol{H} = H_z\mathbf{e}_z$, for various interfacial coupling strengths are presented in Fig. 1. We can see that as J_{int} increases, the hysteresis loop shift also increases and its width decreases until J_{int} is equal to 2% J_{FM}. Beyond this value, there are no hysteresis loops. In Fig. 2 we show the behavior of the corresponding exchange bias and coercive field values, calculated at certain J_{int} values. The exchange bias field increases with a linear dependence on the interfacial exchange parameter. It is larger for the 3.5 nm nanoparticle because in this case it has more uncompensated spins than the 3 nm one. On the contrary, the coercive field decreases as J_{int} increases and it has similar values for both nanoparticles. The results

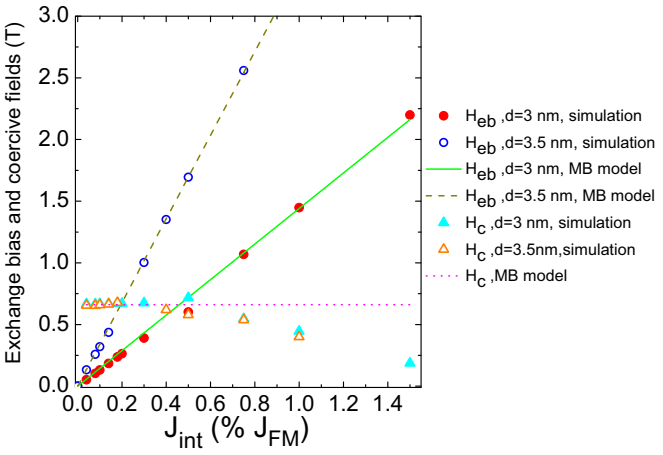

FIG. 2. Dependence of exchange bias and coercive fields on the interfacial exchange coupling for the 3 nm and 3.5 nm nanoparticles. Symbols: Atomistic multispin simulations. Lines: Meiklejohn-Bean model Eqs. (3) and (5).

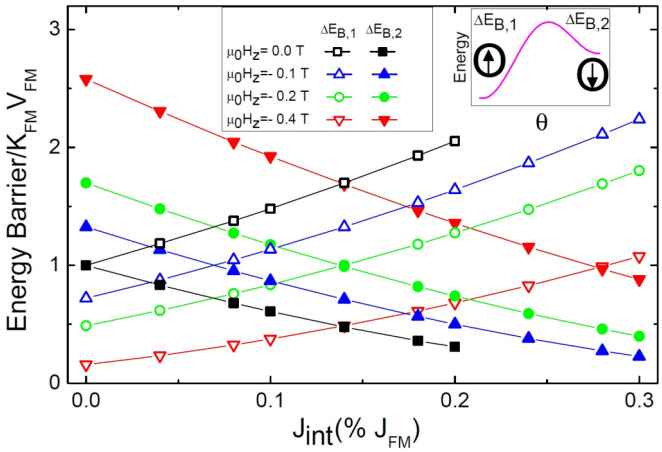

FIG. 3. Dependence of energy barriers of the 3 nm Co/CoO nanoparticle on the interface exchange strength for various applied fields, calculated using atomistic simulations with the Lagrange multiplier method. Inset shows a schematic of the energy landscape profile.

qualitatively coincide with those published by Evans *et al.* [5]. Note also that a linear dependence of the exchange bias field on the interfacial exchange parameter was previously reported by Iglesias *et al.* [9] using Monte Carlo simulations, although for a completely different set of parameters, as discussed in the introduction.

B. Energy barriers

The energy barriers of Co/CoO nanoparticles are obtained by implementation of the Lagrange multiplier method to integrate the constrained dynamical equations, as proposed by Garanin and Kachkachi [10] and further developed by Yanes *et al.* [11]. Briefly, the average magnetization of the particle core is fixed in a desired direction, defined by the polar angle θ_0, and the constraint is taken into account by means of a vector Lagrange multiplier. The constrained energy of the system is then minimized. All the stationary points found by this method coincide with the stationary points of the original Hamiltonian $\mathcal{H}$ since at the stationary points the constrain vanishes. This approach allows one to obtain the energy landscape of the nanoparticle as a function of the polar angle θ_0 from which the two energy barriers are evaluated as functions of the interfacial exchange coupling and the applied field. The first energy barrier $\Delta E_{B,1}$ corresponds to the forward switching, i.e., from the positive saturation magnetization state ($M_{z,FM}/M_{s,FM} \approx +1$, where $M_{z,FM}$ is the z component of macroscopic magnetization of the core and $M_{s,FM}$ is the saturation magnetization of the core) to the negative one ($M_{z,FM}/M_{s,FM} \approx -1$) along the upper hysteresis branch; see inset in Fig. 3. This energy barrier increases with J_{int} due to the influence of the AF shell. The other energy barrier $\Delta E_{B,2}$, separating the (-1) and $(+1)$ states along the lower hysteresis branch, decreases with J_{int}.

The effect of the applied magnetic field is the opposite to the effect of J_{int}, as we can see in Fig. 3, where the first energy barrier decreases and the second one increases. As a result, for small interfacial exchange values (J_{int}) and nonzero field the energy barrier $\Delta E_{B,2}$ is higher than the $\Delta E_{B,1}$, oppositely to the case without external field. As was already noticed by Evans *et al.* [5], the behavior of the energy barriers invalidates the use of exchange-biased nanoparticles for magnetic recording applications, since one of the two energy barriers is always smaller than the zero-field value $\Delta E_B = K_{FM} V_{FM}$, where $V_{FM} = N_{\text{core}} v_0$ is the volume of the core, $K_{FM} = k_{FM}/v_0$ is the macroscopic anisotropy constant of the core, and v_0 is the atomic volume.

III. ANALYTICAL MODEL

In this section we compare the results of our atomistic simulations to the predictions of the Meiklejohn-Bean model [1], which is a mesoscopic model, assuming a macrospin description of the magnetization reversal mechanism. Indeed, Fig. 1 demonstrates that the particle has a hysteresis behavior only for small values of the interfacial exchange parameter ($J_{\text{int}} < 1.6\%\ J_{FM}$). This indicates that we can assume coherent rotation of the core spins, described by a macrospin, and fixed AF spins in the shell. This is also confirmed by a direct analysis of the spin configurations. In this approximation, the multispin Hamiltonian of Eq. (1) is reduced to the following macrospin one:

$$\mathcal{H} \simeq -V_{FM} K_{FM} \cos^2\theta - M_{s,FM} V_{FM} (H_z + H_{eb}) \cos\theta, \tag{2}$$

where θ is the direction of the core macrospin and

$$H_{eb} = \frac{[N_{up} - N_{\text{down}}] J_{\text{int}}}{M_{s,FM} V_{FM}} \tag{3}$$

is the exchange bias field, $K_{FM} = 2.97 \times 10^6$ ergs/cc, $M_{s,FM} = \mu_{FM}/v_0 = 893$ emu/cc, and N_{up} (N_{down}) are the number of "up" ("down") spins at the shell interface in the FC state ($\theta = 0$). The shell interface region contains by definition those spins of the AF shell that couple directly to at least one FM spin in the core. This model states that the exchange bias field is defined by the number of uncompensated spins at the interface. Therefore, in this approximation the atomistic Hamiltonian corresponds to the Stoner-Wohlfarth model with an additional constant field H_{eb} due to the interaction between the core and the shell, which is the exchange bias field. Note that despite the fact that the bias field H_{eb} stems from the exchange coupling at the interface region only, it appears in Eq. (2) to act on all core spins. This corresponds to an assumption of infinite penetration of correlations into the core. Clearly, this approximation fails for large nanoparticles in a multidomain state.

Following the same steps as in the Stoner-Wohlfarth model [12] one can easily find that the energy barriers are given by

$$\frac{\Delta E_{B1,B2}}{V_{FM} K_{FM}} = \left[1 \pm \frac{H_z + H_{eb}}{H_K}\right]^2, \tag{4}$$

where the $(+)$ sign corresponds to the $\Delta E_{B,1}$ value and the $(-)$ sign to the $\Delta E_{B,2}$ value. This model also predicts a coercive field value, independent of the interfacial exchange:

$$H_c = H_K = \frac{2K_{FM}}{M_{s,FM}}. \tag{5}$$

The comparison between the macrospin model and the atomistic (multispin) simulation for the exchange bias and coercive field values is presented in Fig. 2 for the nanoparticles

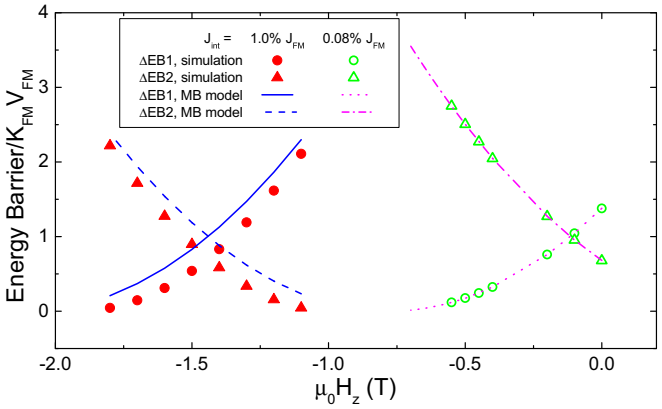

FIG. 4. Comparison between atomistic simulations and the mesoscopic Meiklejohn-Bean model for the field-dependent energy barriers of a 3 nm Co/CoO nanoparticle with $J_{\rm int} = 0.08\% J_{FM}$ and $1.0\% J_{FM}$.

of the two sizes. The agreement for the exchange bias field, with the quantities $N_{\rm up}$ and $N_{\rm down}$ in H_{eb} extracted from the atomistic simulation, is excellent. For the coercive field the macrospin approach coincides quite well with the multispin simulation only in the region where $J_{\rm int}$ is smaller than $0.5\%\ J_{FM}$.

The atomistic simulation results for the energy barriers are compared with the mesoscopic model in Fig. 4. We see that for the case $J_{\rm int} = 0.08\%\ J_{FM}$ the energy barrier calculations from multispin simulation and the mesoscopic model give an excellent agreement. For the interfacial value $J_{\rm int} = 1.0\%\ J_{FM}$, although the results are very similar, the analytical values are somewhat higher than the multispin ones. Looking at the magnetization configuration, we observed some noncollinear core spins close to the interface induced by the AF shell, which decreases the validity of the macrospin approximation. Note, however, that although this interface exchange value is only a small fraction of the core exchange, it produces a large exchange bias since the hysteresis cycle is shifted completely to negative fields and at the remanence there are no two stable configurations. Thus, although the macrospin model gives correct results for values of $J_{\rm int}$ smaller than $0.8\%\ J_{FM}$, for practical purposes it covers the region of interest in terms of the realistic exchange bias values.

IV. DISCUSSION AND CONCLUSIONS

In summary, we have performed atomistic modeling of core-shell magnetic nanoparticles with parameters corresponding to the realistic situation when the AF anisotropy is much smaller than the exchange parameters. Our aim was to calculate the energy barriers for multispin nanoparticles for various interfacial coupling strengths and applied fields. Our results show that exchange biased systems exhibit an increased energy barrier in the upper hysteresis branch ΔE_{B1}, with a corresponding decrease of the barrier in the opposite direction ΔE_{B2}. As a function of the applied field, one of the energy barriers is always smaller than the isolated core energy barrier. Since for magnetic recording applications both energy barriers must be high, it is evident that this situation is not suitable for this purpose. We also established the quadratic scaling of the energy barriers in Co/CoO nanoparticles with the applied field, which is important for practical applications. The multispin calculation showed good agreement with the mesoscopic model of Meiklejohn-Bean [1] that assumes coherent rotation of the (FM) core magnetization and frozen shell (AF) moments. This result justifies the Meiklejohn-Bean model that relates the exchange bias phenomenon to the number of uncompensated spins at the interface. Furthermore, the exchange bias field calculated within the Meiklejohn-Bean model coincides quite well with the multispin simulations for all values of $J_{\rm int}$. At the same time the model predictions for the energy barriers and coercive fields agree with the simulation results in practical cases where $J_{\rm int}$ is smaller than $0.8\%\ J_{FM}$. For larger interface exchange values the approximation of frozen shell and coherent core moments is not satisfactory and a generalization [13] of the original [1] Meiklejohn-Bean model has to be considered.

We anticipate that consideration of a different nanoparticle shape [14] and crystal lattice structure [11] would only modify the number of uncompensated spins and may slightly change the critical values of the exchange parameters, but without introducing qualitatively different results to the ones discussed here.

A final remark is regarding the range of values of the interfacial exchange parameter ($J_{\rm int} \ll J_{FM}, J_{AF}$) for which the exchange bias phenomenon occurs in the present study, as compared to previous works [6]. The exchange bias phenomenon occurs due to the fact that the AF anisotropy (stronger than the FM one) keeps the interfacial spins frozen during the magnetization reversal. For this to happen, the interfacial exchange should be smaller that the AF anisotropy ($J_{\rm int} < k_{AF}$); otherwise drag of interface AF spins by the core spins would occur. Since we adopt here the realistic assumption that $k_{AF} \ll J_{FM}$, then it is reasonable that we observe exchange biasing for interface exchange values from 100 to 1000 times smaller than the FM exchange ($J_{\rm int} \ll J_{FM}$). This also defines the limit of validity of the Meiklejohn-Bean model; namely, the regime where the drag of the AF spins occurs corresponds to the interfacial exchange parameter comparable to the AF anisotropy value. On the contrary, in previous studies [6] it was taken as $k_{AF} \sim J_{FM}$ and thus the interfacial exchange parameter had to be in the same range ($J_{\rm int} \sim J_{FM}$) for exchange biasing to occur. In this case one expects AF spin drag to occur and the conditions of the Meiklejohn-Bean model (i.e., rigid shell) are seriously violated. In realistic cases various inevitable imperfections (lattice mismatch, interface alloying and roughness, etc.) would lead to weak (effective) interface coupling, providing further support to our interfacial parameters.

We should finally mention that in our study we did not consider the possibility of strong surface anisotropy. For thin shells, strong perpendicular surface anisotropy would increase the effective shell anisotropy value, leading to a wider range of $J_{\rm int}$ values for which the Meiklejohn-Bean model is valid.

ACKNOWLEDGMENT

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