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Magnetization curling in elongated heterostructure particles

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A rigorous micromagnetic study of nucleation by use of the magnetization curling mode in an elongated particle with heterostructure is presented. We categorize the heterostructure particles into three different types depending on their growth conditions and internal structures. The coercivity of the heterostructure particles critically depends on the relative magnetic parameters of the composite materials. The physical origins of the enhanced coercivity for the three types of heterostructure particles are quite different. The initial slope of the enhanced coercivity of surface-coated particles results from the shell crystalline anisotropy, while the saturation level depends on the interfacial coupling, shell crystalline anisotropy, and shell surface anisotropy. The main contribution to the enhancement of the coercivity of surface-modified particles is the surface anisotropy of the adsorbed layer at the particle surface. The homogeneity of the doped materials within the volume-modified particles affects their coercivity and the saturation level of the coercivity is always higher than that of the other two types. Agreement between theory and experiment is reasonably good.

I. INTRODUCTION

Heterostructure particles are frequently used in advanced magnetic data-storage technology for their superior magnetic properties, and they have attracted considerable experimental and industrial interest.[1-10] The large magnetic moment yields a high signal level and the coercivities obtainable allow for high bit densities. Experimental and theoretical investigations are under way to understand the origin of the high coercivity, and the knowledge derived from these studies can be used to improve the magnetic properties of heterostructure particles further. Depending on their growth conditions and internal structures, elongated particles with heterostructure can usually be classified into three different types in terms of magnetic recording:[6] surface-coated particles [e.g., Co-surface-coated (epitaxial) iron oxide particles], surface-modified particles (e.g., Co-surface-adsorbed iron oxide particles), and volume-modified particles (e.g., Co-surface-doped and Co-substituted or doped iron oxide particles). In general, the modification alters the magnetic properties on or near the surface of the precursor particles in surface-treatment techniques, and throughout the whole volume in volume-modification techniques.

Several analytic models have been proposed to study the magnetization curve and nucleation of magnetization reversal of surface-coated particles.[8,10] However, there exists no satisfactory theory regarding the enhancement of coercivity even for this type of heterostructure particles. The origin of this enhancement has been qualitatively attributed to many different mechanisms, e.g., volume averaging,[8] interfacial exchange coupling,[10] magnetostriction,[11] and reduced demagnetization.[12] These mechanisms share the common assumption that there must be uniform magnetization in order to explain the enhancement of coercivity. Nevertheless, some recent numerical results show that the reversal mode is nonuniform.[13] Moreover, experimental data show that cobalt-modified ion oxide particles seem to favor the incoherent reversal of magnetization.[1,14] Therefore, the model of rotation in unison may not be appropriate for these heterostructure particles.

Besides the numerical calculations,[13] the atomic-layer model (ALM), which treats the particles as composed of concentric layers each approximately one lattice spacing thick,[15,16] has been proposed to analyze the possibility of a nonuniform reversal mechanism for surface-coated particles. An advantage of the ALM is the easy incorporation of arbitrary radial inhomogeneities of the material parameters; however, it can only be applied to some simple cases because of the complicated numerical calculations. Moreover, it is not easy to understand the underlying physics of the reversal mechanism just from numerical results. Another theoretical approach to the nonuniform magnetization reversal in coated particles (e.g., Co-surface-coated γ-Fe_2O_3 particles), based on Brown's equation with appropriate boundary conditions, has shown that a curling mode probably occurs during the reversal.[17] However, these results show a much earlier saturated behavior of the nucleation field within the coated thickness than is observed, and one can only qualitatively explain the coercivity increase of coated particles. The demerit of this simple curling model is that it takes the coating into account only as a shell anisotropy term, and neglects the possibilities of spatial variation of magnetization and exchange constant. Moreover, the assumption of smoothly changing magnetic moment across the interface, which implies an infinite interfacial exchange coupling,[18] is doubtful; the contribution of magnetic surface anisotropy[19] is disregarded altogether for simplicity. Ex-

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perimental data for cobalt-treated iron oxides show that approximately one monolayer of Co atoms is responsible for the significant enhancement of the coercivity.[5] This fact suggests that interfacial effects may play an important role. An extension of this micromagnetic continuum theory with the extra consideration of core-shell interfacial coupling and shell surface anisotropy can qualitatively explain the surface-coated particles successfully;[18] however, the particles are still characterized only by parameters which are homogeneous within the core and shell regions, and the theory is only appropriate for surface-coated particles. Nevertheless, these curling models results in analytical expressions and one can easily understand the origins of the magnetic behavior for the heterostructure particles.

Although much effort has been devoted to understanding the reversal mechanism and nucleation in heterostructure particles, the origins of their improved magnetic properties are still not clarified. In particular, all the above theoretical models and numerical simulations concentrate only on the mechanism for surface-coated particles, and a reversal theory for surface-modified and volume-modified particles is lacking. Moreover, the possibility of inhomogeneous magnetic parameters of the heterostructure particles is neglected for simplicity. From a theoretical point of view, the heterostructure particle leads to an inhomogeneous micromagnetic problem and, for some special geometry, can be solved rigorously.[17,18] When a ferromagnetic particle is saturated in a large magnetic field, and the applied field is slowly reduced and then reversed, the magnetization will start to reverse in a well-defined field called the nucleation field. This field is an eigenvalue of a set of differential equations, and may be found rigorously, as has been done in some cases.[20]

The determination of coercivity actually requires calculation into the nonlinear regime, but most of the previous methods are restricted to a linearized method for simplicity.[14,17,18] Strictly speaking, such methods allow one only to calculate the nucleation field, but not the coercivity. However, for an infinite solid cylinder, it has been shown numerically that the curling solution of the linearized Brown's equation is not a stable solution of the full nonlinear Brown's equation at applied fields larger than the nucleation field, and the only possible stable states are thus those of uniform alignment, depending on the orientation of the reversing field.[21] Thus, the magnetization was assumed to reverse completely in a single step at the nucleation field, and the conclusion was that the magnetization curve of an infinite isotropic ferromagnetic cylinder has a rectangular hysteresis loop. In other words, the coercive force can be given by the nucleation field.[22] Actually, the linearized method was successfully used to explain the size and angular dependence of the coercivity for small particles,[14,23] and the successes of the nucleation-field calculation in explaining experimental coercivity data suggest this to be a profitable approach, at least in some cases.

In this paper, we treat heterostructure particles as infinite circular cylinders with inhomogeneous magnetic properties.[24] Rigorous solutions, for the curling mode, to the linearized Brown differential equation of the infinite cylinder with inhomogeneous magnetic properties are presented. Thus, we can handle either surface-treated or volume-modified particles rigorously. The remainder of the paper is outlined as follows. We categorized the elongated particles with heterostructure into three different types: surface coated, surface modified, and volume modified. In Sec. II the theories of these three different types based on micromagnetic curling are presented, the basic formulas for the nucleation field are derived, and the nature of our assumptions is discussed. Numerical results are presented and discussed in Sec. III. Finally, we give a detailed comparison of our theoretical calculations with experimental data.

II. BROWN'S EQUATIONS FOR HETEROSTRUCTURE PARTICLES

An elongated particle with heterostructure leads to an inhomogeneous micromagnetic problem which can be solved rigorously for some specific particle shapes, e.g., an infinite cylinder.[24] Because of the growth conditions and internal structures, elongated particles with heterostructure can be classified into three different types:[6] surface-coated particles [e.g., Co-surface-coated (epitaxial) iron oxide particles], surface-modified particles (e.g., Co-surface-adsorbed iron oxide particles), and volume-modified particles (e.g., Co-surface-doped and Co-substituted or -doped iron oxide particles). Brown's equations for each type can then be derived accordingly.

A. Surface-coated particles

The structure of surface-coated particles can usually be divided into two distinct regions: core and shell, e.g., for cobalt-coated epitaxial γ-Fe_2O_3 particles.[2,6,8] Thus, we can simulate this kind of heterostructure particle as an infinite circular cylinder of two parts: the core part: $0 \le r < R_1$ and the shell part: $R_1 \le r < R_2$, where R_1 and R_2 are the core and shell radii, respectively. The magnetic properties are generally different for the two regions and can be treated as a stepwise distribution function of radius. The effect of the interface between core and shell is phenomenologically imposed by an interfacial coupling interaction,[10] and the contribution of shell surface anisotropy is also considered. Therefore, the free energy per unit (cylinder axis) length for a coated particle is

$$
\begin{aligned}
E = {} & 2\pi \int_0^{R_1} \left[A_1 \left[\frac{d\theta_1}{dr} \right]^2 + A_1 \frac{\sin^2\theta_1}{r^2} + K_1 \sin^2\theta_1 - H_a M_1 \cos\theta_1 \right] r\,dr \\
& + 2\pi \int_{R_1}^{R_2} \left[A_2 \left[\frac{d\theta_2}{dr} \right]^2 + A_2 \frac{\sin^2\theta_2}{r^2} + K_2 \sin^2\theta_2 - H_a M_2 \cos\theta_2 \right] r\,dr \\
& - (4\pi R_1 A_i / d) \cos(\theta_{1i} - \theta_{2i}) + 2\pi K_{2S} (R_1 \sin^2\theta_{2i} + R_2 \sin^2\theta_{2b}) \ , \qquad (1)
\end{aligned}
$$

where the subscripts $j=1,2$ refer to the core and shell; and A_j, K_j, and M_j are the exchange constants, uniaxial crystalline anisotropy constants, and magnetizations of the two regions, respectively. The angles θ_j of the magnetizations are taken with respect to the cylinder axis. Subscripts i and b refer to the physical core-shell interface at $r=R_1$, and the outer surface at $r=R_2$, respectively. A_i is the interfacial exchange constant,[10] d is the atomic lattice spacing at the interface, and K_{2S} is the postulated uniaxial surface anisotropy constant of the shell.[19]

Applying variational methods to minimize the above energy functional yields the following Euler differential equations

$$\frac{d^2\theta_1}{dt^2}+\frac{1}{t}\frac{d\theta_1}{dt}-\left[\frac{\cos\theta_1}{t^2}+\pi S_1^2(h+g_1\cos\theta_1)\right]\sin\theta_1 =0 \quad \text{for } 0\le t\le 1\ , \tag{2a}$$

$$\frac{d^2\theta_2}{dt^2}+\frac{1}{t}\frac{d\theta_2}{dt}-\left[\frac{\cos\theta_2}{t^2}+\pi S_1^2\frac{q}{p}\left[h+\frac{g_2}{q}\cos\theta_2\right]\right]\sin\theta_2 =0 \quad \text{for } 1\le t\le T\ . \tag{2b}$$

Here we use reduced units as follows: $t=r/R_1$, $T=R_2/R_1$, $S_1=R_1M_1/A_1^{1/2}$, $h=H_a/(2\pi M_1)$, $g_j=K_j/(\pi M_1^2)$, $p=A_2/A_1$, and $q=M_2/M_1$. The boundary conditions at the interface and outer surface are

$$\frac{d\theta_{1i}}{dt}=\alpha_i\sin(\theta_{2i}-\theta_{1i})\ , \tag{3a}$$

$$\frac{d\theta_{2i}}{dt}=p^{-1}\alpha_i\sin(\theta_{2i}-\theta_{1i})+\tfrac{1}{2}\beta_{2S}\sin(2\theta_{2i})\ , \tag{3b}$$

$$\frac{d\theta_{2b}}{dt}+\tfrac{1}{2}\beta_{2S}\sin(2\theta_{2b})=0\ , \tag{3c}$$

where $\alpha_i=R_1A_i/(A_1d)$ and $\beta_{2S}=R_1K_{2S}/A_2$. The nucleation field can be found by linearizing Eqs. (2) around the solution $\theta=0$ and solving them with respect to the boundary conditions (3). The linearized equations are Bessel equations with solutions

$$\theta_1(t)=C_1J_1(\mu t)\ , \tag{4a}$$

$$\theta_2(t)=\begin{cases} C_2I_1(\nu t)+C_3K_1(\nu t), & h+g_2/q>0\ ,\\ C_2J_1(\nu t)+C_3Y_1(\nu t), & h+g_2/q<0\ ,\end{cases} \tag{4b}$$

where J_1 and Y_1 are Bessel functions of the first and second kind, I_1 and K_1 are modified Bessel functions, C_j are arbitrary integration constants $\ll 1$, and

$$\mu=[-\pi S_1^2(h+g_1)]^{1/2}\ , \tag{5a}$$

$$\nu=\left[\pi S_1^2\frac{q}{p}\left|h+\frac{g_2}{q}\right|\right]^{1/2}\ . \tag{5b}$$

Nontrivial solutions satisfying the condition (3) exist if

$$\begin{vmatrix} \mu J_1'(\mu)+\alpha_iJ_1(\mu) & -\alpha_iF_1(\nu) & -\alpha_iG_1(\nu)\\ p^{-1}\alpha_iJ_1(\mu) & \nu F_1'(\nu)-\Omega F_1(\nu) & \nu G_1'(\nu)-\Omega G_1(\nu)\\ 0 & \nu F_1'(\nu T)+\beta_2F_1(\nu T) & \nu G_1'(\nu T)+\beta_2G_1(\nu T)\end{vmatrix}=0\ , \tag{6}$$

where $\Omega=p^{-1}\alpha_i+\beta_2$, and the functions F and G represent I_1 and K_1 if $h+g_2/q>0$ or J_1 and Y_1 if $h+g_2/q<0$, respectively. By evaluating the least negative root of the determinant (6), one can find the nucleation field h_n at which reversal starts.

B. Surface-modified particles

Iron oxide particles with adsorbed cobalt are prepared in such a way that there exists only a thin surface layer of Co- ferrite and the preferred orientation of the cobalt ions at the surface is parallel to the long axis.[2,7,9] Therefore, the contribution to crystalline anisotropy due to the cobalt ions at the surface can be viewed as a pure surface effect. Here, we treat this kind of particle as an infinite circular cylinder with uniform magnetic properties but with extra anisotropy at the surface.[2,7,9] The free-energy density is

$$E=2\pi\int_0^R\left[A\left[\frac{d\theta}{dr}\right]^2+A\frac{\sin^2\theta}{r^2}+K_1\sin^2\theta -H_aM_s\cos\theta\right]r\,dr+2\pi RK_s\sin^2\theta_b\ , \tag{7}$$

where R, A, M_s, and K_1 are the radius, exchange constant, magnetization, and uniaxial crystalline anisotropy constant of the particle, respectively. K_s is the uniaxial surface anisotropy constant, and subscript b represents the outer surface of the particles, i.e., $r=R$.

Following the same procedure as described above, we obtain the linearized Euler differential equation and the boundary condition:

$$\frac{d^2\theta}{dt^2}+\frac{1}{t}\frac{d\theta}{dt}-\left[\frac{1}{t^2}+\pi S^2(h+g)\right]\theta=0\ , \tag{8a}$$

$$\frac{d\theta_b}{dt}+\beta_s\theta_b=0\ , \tag{8b}$$

where $t=r/R$, $S=RM_s/A^{1/2}$, $g=K_1/(\pi M_s^2)$, $h=H_a/(2\pi M_s)$, $\beta_s=RK_s/A_b$. Thus,

$$\theta(t)=CJ_1(\omega t)\ , \tag{9a}$$

$$\omega J_1'(\omega)+\beta_sJ_1(\omega)=0\ , \tag{9b}$$

where $\omega=[-\pi S^2(h+g)]^{1/2}$, J_1 is a Bessel function of the first kind, and C is an arbitrary integration constant $\ll 1$. By evaluating the least negative root of Eq. (9b), one can find the nucleation field h_n at which reversal starts.

C. Volume-modified particles

To produce volume-modified particles foreign material is doped into the precursor particles, with the concentration of the doped material usually being higher near the surface. The magnetic properties of the volume-modified particles therefore are not uniform.[6,25] For this type of particle, the magnetic parameters change along the radial direction, and the free-energy density can be written as

$$E=2\pi\int_0^R\left[A(r)\left[\frac{d\theta}{dr}\right]^2+A(r)\frac{\sin^2\theta}{r^2}+K_1(r)\sin^2\theta\right.$$
$$\left.-H_aM(r)\cos\theta\right]r\,dr+2\pi RK_s\sin^2\theta_b\ , \quad (10)$$

where R, $A(r)$, $K_1(r)$, and $M(r)$ are the radius, exchange constant, uniaxial crystalline anisotropy constant, and magnetization of the modified particles, respectively. K_s is the postulated uniaxial surface anisotropy constant and subscript b refers to the outer surface of the particles. The linearized Euler equation is

$$A(t)\frac{d^2\theta}{dt^2}+\left[\frac{A(t)}{t}+\frac{dA(t)}{dt}\right]\frac{d\theta}{dt}$$
$$-\left[\frac{A(t)}{t^2}+K_1(t)R^2+\tfrac{1}{2}H_aM(t)R^2\right]\theta=0\ , \quad (11a)$$

and the boundary condition is

$$\frac{d\theta_b}{dt}+\beta_s\theta_b=0 \text{ at } t=1\ , \quad (11b)$$

where $t=r/R$ and $\beta_s=RK_s/A(t=1)$. If A, K, and M are uniform, the results can be reduced to those for surface-adsorbed particles. If we let

$$A(t)=A_0+\Delta A(t)\ ,$$
$$K_1(t)=K_{1,0}+\Delta K_1(t)\ , \quad (12)$$
$$M(t)=M_0+\Delta M(t)\ ,$$

where subscript 0 refers to the unmodified particles, Eq. (11a) can be rewritten as

$$(1+a)\frac{d^2\theta}{dt^2}+\left[\frac{1+a}{t}+\frac{da}{dt}\right]\frac{d\theta}{dt}$$
$$-\left[\frac{1+a}{t^2}+Q_{1,0}+\Delta Q_1+Q(1+m)\right]\theta=0\ , \quad (13)$$

where $a=\Delta A/A_0$, $m=\Delta M/M_0$, $Q_{1,0}=R^2K_{1,0}/A_0$, $\Delta Q_1=R^2\Delta K_1/A_0$, and $Q=H_aM_0R^2/(2A_0)$. In general, the analytical solution of Eq. (13) cannot be obtained and one should resort to some numerical method (e.g., Runge-Kutta).

III. NUMERICAL RESULTS AND DISCUSSION

A. Surface-coated particles

The influence of the shell exchange constant on the nucleation field is shown in Fig. 1. For a thin shell, the effect of stepwise variation of the exchange constant is very small; but for a thick shell this effect becomes significant. The larger the shell exchange constant the higher the nucleation field for a thick shell. However, the shell magnetization affects the nucleation field in an opposite manner (Fig. 2): For a shell of smaller magnetization, we must apply a larger external field to induce instability; therefore, the heterostructure particle has a higher nucleation field. It is well known that in a single-domain, homogeneous ferromagnetic cylinder a large exchange constant or a small magnetization result in a higher nucleation field according to the magnetization curling theory.[26] When this single-domain particle is coated with a shell of large exchange constant, the magnetic moments in the shell region will be more tightly coupled to resist the early reversal of the core region; therefore, the coated particle will have a higher nucleation field. When a particle is coated with a shell of large magnetization, it will induce a large Zeeman energy in the presence of an external field antiparallel to the magnetization. Thus, it is certainly easier to overcome the energy barrier and then to induce instability for the coated particles. In other words, the coated particles have a smaller nucleation field than do the unmodified particles.

We have also studied the effect of interfacial coupling strength α_i. It is seen from Fig. 3 that the nucleation field increases with increasing interfacial coupling strength and shell thickness, and that it saturates at large values of α_i or beyond a certain shell thickness. For a thin shell the nucleation field saturates at a weak interfacial coupling strength, while for a thick shell it requires a stronger interfacial coupling strength to saturate. Figure

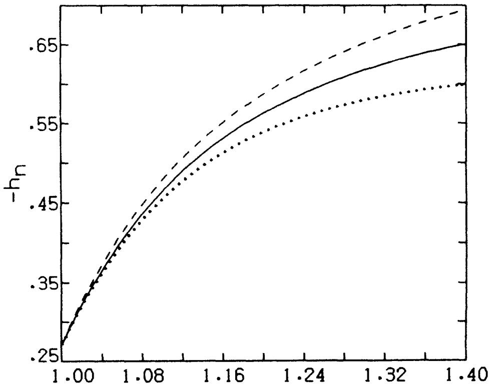

FIG. 1. Influence of the exchange constant of the shell on the relation between the reduced nucleation field h_n and the ratio of R_2 to R_1. R_1 and R_2 are the core and shell radii, respectively. $S_1=2.0$, $q=1$, $g_2=1.2$, $g_1=\beta_{2s}=0$, and $\alpha_i=1000$, and $p=0.5$, 1.0, 2.0 from bottom to top, respectively. The larger the exchange constant of the shell, the higher the nucleation field.

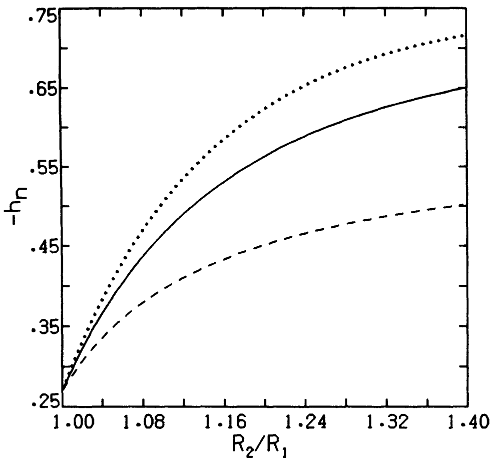

FIG. 2. Influence of shell magnetization on the relation between the reduced nucleation field h_n and the ratio of R_2 to R_1. $S_1=2.0$, $p=1$, $g_2=1.2$, $g_1=\beta_{2s}=0$, and $\alpha_i=1000$, and $q=2.0$, 1.0, 0.5 from bottom to top, respectively. The smaller the shell magnetization, the higher the nucleation field.

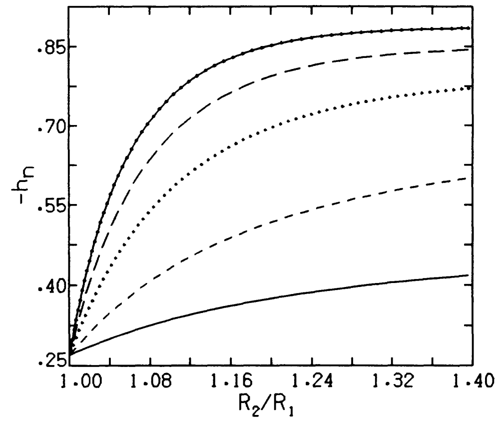

FIG. 4. Influence of shell crystalline anisotropy on the relation between the reduced nucleation field h_n and the ratio of R_2 to R_1. $S_1=2.0$, $p=q=1$, $\alpha_i=1000$, $g_1=\beta_{2s}=0$, and $g_2=0.5$, 1.0, 2.0, 3.0, 4.0 from bottom to top, respectively. The larger the shell crystalline anisotropy, the higher the nucleation field and the initial slope.

3 also clearly shows that the initial slope of the nucleation field versus shell thickness is insensitive to the interfacial coupling strength except for the case of rather small α_i. From Eqs. (3), we know that a finite value of interfacial coupling strength permits significant slippage between θ_{1i} and θ_{2i}. This slippage gradually decreases as α_i increases, and finally disappears as α_i approaches infinity. This is the reason that the core-shell interface is essentially absent in Aharoni's calculations.[17] The effect of the shell crystalline anisotropy on nucleation field is illustrated in Fig. 4. The nucleation field of coated particles initially increases linearly with increasing shell thickness, and tends then toward a constant value. The saturation level and the initial slope increase with increasing shell anisotropy constant; nonetheless, the saturation threshold decreases with increasing shell anisotropy constant.

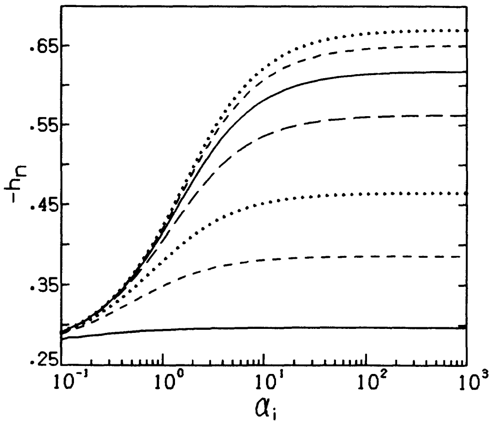

FIG. 3. Relation between the reduced nucleation field h_n and the interfacial coupling strength α_i for different ratios of R_2 to R_1. $S_1=2.0$, $p=q=1$, $g_1=0$, $g_2=1.2$, $\beta_{2s}=0$, and $T(=R_2/R_1)=1.01$, 1.05, 1.1, 1.2, 1.3, 1.4, 1.5 from bottom to top, respectively.

Finally, the effect of the shell surface anisotropy is studied. The surface anisotropy has been shown to be thickness dependent,[27] and the surface anisotropy constant can be approximately expressed[18] as $K_{2s}^{m}\exp(-t_c/t)$, where t is the shell thickness and t_c some characteristic thickness. The effect of shell surface anisotropy comes into play only if the shell is thick enough, and the saturation threshold depends on the characteristic thickness [Fig. 5(a)]. Experimentally, it is known that the shell does not form completely but is composed of islandlike regions appearing on the core surface for a small shell thickness. When K_{2s}^{m} increases, the nucleation field increases only above a critical shell thickness [Fig. 5(b)].

B. Surface-modified particles

The solution of Eq. (9b) is shown in Fig. 6 where the nucleation field initially rapidly increases with surface anisotropy constant and then gradually tends toward a constant value. No matter how large the surface anisotropy constant is, the enhancement of the nucleation field cannot exceed a certain upper bound. For single-domain particles, it is well known that nucleation through curling always results from a large deviation of magnetization at the surface.[26] However, the surface anisotropy of the surface-modified particles can stabilize the instability of the magnetization at the surface, i.e., the surface magnetization maintains its original value until a larger reverse field is applied. As the surface anisotropy increases, the magnetic moments at the surface are more reluctant to tilt and the nucleation region[28] shifts radially inwards, and thus the nucleation field increases. Finally, when the surface anisotropy becomes infinite, the moments at the surface stop tilting even at the nucleation field, and the nucleation field achieves its maximum. From Fig. 6, we see that the value of ω is between 1.8412 and 3.8317 as β_s varies from zero to infinity. Thus, the maximum value for the enhancement of the nucleation field is $22.6A/(R^2M_s)$. This surface effect is substantially different from the contribution of the bulk uniaxial crystalline anisotropy, which enhances the nucleation field linearly and is size independent.[29] Obviously, the smaller the particle size, the stronger the surface effect.

C. Volume-modified particles

The effect of the spatial variation of magnetic properties in volume-modified particles has also been investigated. If the doping influences the magnetic properties uniformly within the volume-modified particles, we can treat this kind of particle like surface-adsorbed particles and solve the problem analytically. However, because of the growth conditions and the diffusion of dopant, the magnetic properties vary along the radial direction and we assume for them the usual power law:

$$f(t)=f_{\max}t^{l}\,, \tag{14}$$

where the symbol f can represent a, ΔQ_1, or m, respectively. First, we only consider the effect of variation of the exchange constant a. When $a_{\max}$ is positive, the nu-

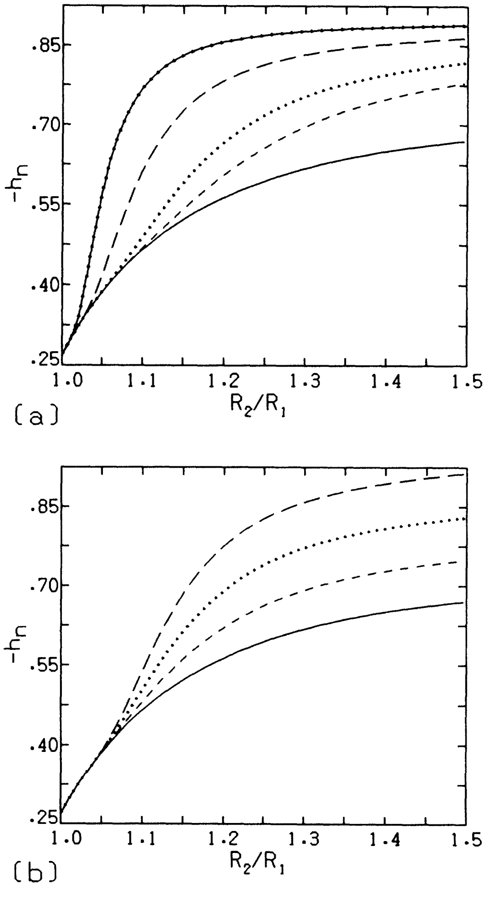

FIG. 5. Influence of shell surface anisotropy on the relation between the reduced nucleation field h_n and the ratio of R_2 to R_1. $S_1=2.0$, $p=q=1$, $g_1=0$, $g_2=1.2$, and $\alpha_i=1000$. (a) $\beta_{2s}^{m}=5$, and $t_c=\infty$, 0.6, 0.4, 0.2, 0.1 from bottom to top, respectively; (b) $t_c=0.35$, and $\beta_{2s}^{m}=0$, 2, 5, 10 from bottom to top, respectively. The shell surface anisotropy will further increase the nucleation field for thick coating.

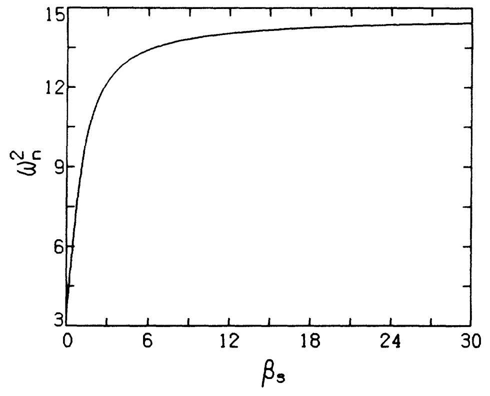

FIG. 6. ω_n^2 versus reduced surface anisotropy β_s. $\omega_n^2=-\pi S^2(h_n+g)$, and $\beta_s=RM_s/A_b$.

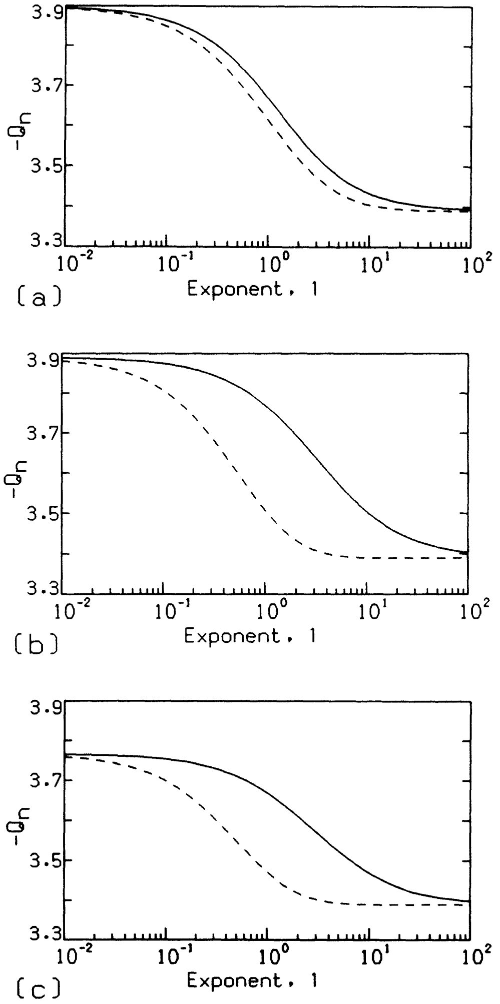

FIG. 7. Nucleation field Q_n versus the exponent l in the power law for spatial variation of exchange constant (a), anisotropy constant (b), and magnetization (c). Solid curves and dashed curves indicate the results due to Eqs. (14) and (15), respectively. (a) $a_{\max}=0.15$ and $Q_1=m=\beta_s=0$; (b) $a_{\max}=m=Q_{1,0}=\beta_s=0$, and $\Delta Q_1=0.5$; (c) $a_{\max}=Q_1=\beta_s=0$, and $m=-0.1$.

cleation field increases as the power l decreases, as expected [see Fig. 7(a)]. The influence of the variation of crystalline anisotropy ΔQ on the nucleation field is similar to that of the exchange constant [see Fig. 7(b)]; while the effect of the variation of magnetization m for nucleation field is the opposite [see Fig. 7(c)]. To understand the role of the dopant near the particle center, we use another kind of power law, i.e.,

$$f(t)=f_{\max}(1-t)^l . \qquad (15)$$

For the variation of the exchange constant, the nucleation field due to Eq. (15) is always somewhat smaller than that due to Eq. (14), but the difference is small. Similar results hold also for the variation of magnetization and anisotropy; however, the disparity is apparently much larger than that for the exchange constant. This implies that, if one cannot modify the magnetic properties uniformly, (1) the effect of variation of magnetic properties near the surface of the doping materials is greater than that near the particle center; and (2) changing the properties of magnetization and anisotropy near the particle surface is a more efficient method to enhance the nucleation field, or coercivity.

IV. COMPARISON OF THE THEORETICAL AND EXPERIMENTAL RESULTS AND CONCLUSIONS

From the above studies we can clarify the origins of the coercivity enhancement for the three different types of heterostructure particles. The application of the present model to a real elongated heterostructure particle is demonstrated as follows. For Co-modified γ-Fe_2O_3 particles, experimental results show that there exist large differences between the saturation behavior in adsorbed and epitaxial particles: a complete saturation at about 2–4 wt % Co in the former case[2,7,9] and 40 wt % Co in the latter case.[8] Moreover, the coercivity of volume-modified particles is even higher.[6] The reasons for these differences will be elucidated in the following discussion.

For epitaxial Co ferrite on γ-Fe_2O_3 particles, the precursor particles are dispersed in a solution containing both Co^{2+} and Fe^{2+} ions;[2,4,8] therefore, an epitaxial layer of Co ferrite is formed and encircles the precursor particle. This kind of particle thus consists usually of a core and a shell region. The anisotropy of the cobalt ferrite shell seems to be uniaxial, with the easy axis parallel to the long axis of the particles.[2,4,8] The origin of the uniaxial anisotropy is still not quite clear; it has been proposed that the preferred orientation of Co^{2+} ions is due to the influence of the magnetic field produced by the inner core of iron oxide.[8] Another possibility is that the disordered alignment of cobalt ferrite crystallites in the surface layer[7] induces a uniaxial anisotropy constant of 5×10^5 erg/cm^3.[4] Experimental data show that the magnetization of γ-Fe_2O_3 and $CoFe_2O_4$ are almost the same, but the Curie temperatures are different, implying that the exchange constants for the two materials are also different. A rough estimate tells us that the exchange constant is proportional to the product of the Curie temperature and the inverse of the distance between neighboring magnetic moments, if we suppose that all moments are located at the lattice sites of a simple cubic crystal structure. Thus, the ratio of the exchange constants p is about 0.83.

For particles with adsorbed cobalt, the precursor particles are dispersed in a solution containing only Co^{2+} ions. Therefore, a Co ferrite layer is formed at the particle surface and then slows down further growth of Co ferrite inside the particles. Actually, this process is quite similar to that for passivated iron particles.[30]

During the Co ferrite formation, the preferred orientation of the cobalt ions at the surface is parallel to the long axis and an induced uniaxial surface anisotropy appears.[2,7,9] The maximum value of the surface anisotropy constant can be estimated as $K_s^{\max}=K_u\delta$, where K_u is the induced uniaxial anisotropy constant in the epitaxial particles and δ is the size of a Co ferrite molecule. The numerical value of $\beta_s^{\max}$ is about 0.3 if values of $\delta=2.5$ Å, $R=0.025$ μm, $M_s=350$ emu/cm^3, $S=2.5$, and $K_u=0.5\times10^6$ erg/cm^3 are used. When the weight ratio of Co to γ-Fe_2O_3 increases, the number of $CoFe_2O_4$ molecules increases till they completely cover the precursor-particle surface. Qualitatively, the effective surface anisotropy constant increases with increasing cobalt content and gradually saturates. For the best fit to the experimental data,[2,7,9] the relation between surface anisotropy and weight ratio can be roughly approximated as

$$K_s(w)=K_s^{\max}[1-\exp(-w/w_c)] ,$$

where w_c is a characteristic weight ratio.

For cobalt-volume-doped γ-Fe_2O_3 particles, the Co ions are dispersed throughout the whole volume of the particles and substitute for Fe on B sites or fill B-site vacancies. It is known that, in bulk, the magnetic anisotropy of Co ferrite is a cubic magnetocrystalline anisotropy with $\langle 100\rangle$ easy directions of magnetization introduced by the cobalt ions. However, when the cobalt content is very small, the uniaxial shape anisotropy is stronger than the cubic crystalline anisotropy.[31] It has been shown[32] that, as long as the uniaxial anisotropy constant is larger than the cubic anisotropy constant, the direction of minimum energy for magnetization deviates but little from that for uniaxial anisotropy. Therefore, instead of cubic anisotropy, we may still use the effective uniaxial anisotropy K_u, which depends on the Co molar ratio, measured by Bozorth, Tilden, and Williams[33] in polycrystalline samples. This dependence has been approximately written as[16] $K_u(x)=K_{u,m}fx^u\exp[-(x/b)^n/n]$, where $K_{u,m}=2.16\times10^6$ erg/cm^3, $u=1.32$, $b=0.7$, $n=7.5$, and $f=1.82$.

With the above experimental information for cobalt-modified γ-Fe_2O_3 particles, we can then utilize the present theory to study their reversal properties. As indicated in Fig. 8, the coercivities[34] of both adsorbed and epitaxial particles increase with increasing cobalt content and gradually saturate for large cobalt content. However, both the saturation level and the saturation threshold of adsorbed particles are smaller than those of epitaxial particles as the cobalt content varies. For the volume-doped particles, the coercivity increases quasilinearly with cobalt content, at least for the observed weight per-

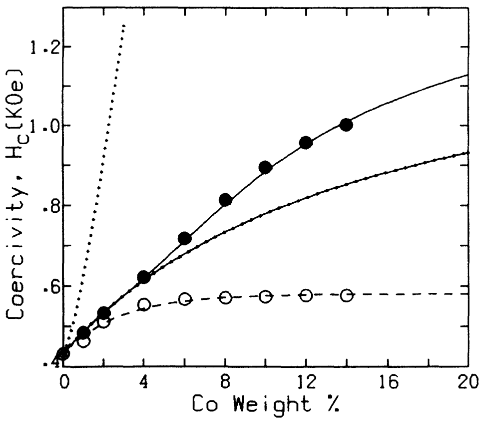

FIG. 8. Coercivity versus Co wt % in γ-Fe_2O_3 for three kinds of cobalt-modified γ-Fe_2O_3 particles. The dashed, solid, and dotted lines are obtained from theoretical results for surface-modified, surface-coated, and volume-modified particles, respectively. The open circles and solid circles refer to experimental data for γ-Fe_2O_3 particles with surface-adsorbed and surface-epitaxial cobalt (Ref. 2), respectively. The solid line with dots refers to the simple curling model without shell surface anisotropy or spatial variation of the exchange constant. The fitting parameters are mentioned in the text.

centages. This theoretically predicted behavior agrees qualitatively with the experimental results.[6] The parameter S is chosen to be 2.06 for the precursor particle with aspect ratio 8 and magnetization 350 emu/cm^3.[2] Also, the following parameters are used to fit the experimental data: $p=0.83$, $q=1$, $g_1=0$, $g_2=0.9$, $\beta_{2s}^m=2.3$, and $t_c=0.25$ for surface-coated particles; $\beta_s=0.16$ and $w_c=2.8\%$ for surface-modified particles; and $a=m=Q_{1,0}=\beta_s=0$ for volume-modified particles.[35] The results of Aharoni's curling model[17] for coated particles are also plotted for comparison. Clearly, the physical origins of the coercivity enhancement in the three types of heterostructure particles are quite different. The main contribution to the coercivity of surface-modified particles is the surface anisotropy of the adsorbed layer. The initial slope of increasing coercivity of the surface-coated particles results from the shell crystalline anisotropy, while the saturation level depends on the interfacial coupling and the shell crystalline anisotropy. The shell surface anisotropy will further increase the coercivity for thick coating. The homogeneity of the doped materials within the volume-modified particles affects the coercivity, and its saturation level is always higher than in the other two types.

In this paper, we have developed a micromagnetic theory of nucleation using the magnetization curling mode in an elongated particle with heterostructure. The theory takes into account the spatial variation of magnetic material parameters (e.g., exchange constant, magnetization, crystalline anisotropy, and surface anisotropy) and is therefore more realistic and better applicable to elongated heterostructure particles than previous theories. Actually, our model is strictly valid only for calculation of the nucleation field; however, we compare our results with the coercivity, which usually requires fully nonlinear calculations. Although there exists evidence that these two quantities are in some cases equal,[21,22] it is still questionable whether our model is applicable to such heterostructure particles or not. Nevertheless, a fully dynamic, nonlinear reversal theory of magnetization after nucleation is still missing at present, and it seems reasonable to understand the origins of the coercivity enhancement of heterostructure particles from a linear theory, as it has proved to be very successful in many cases. In our numerical fittings, we adjust the value of the shell anisotropy so that the value of the coercivity is close to the experimental data. We thus regard our approach as phenomenological also. Nevertheless, we have successfully explained the origins of coercivity enhancement for three kinds of cobalt-modified particles: Volume-doped, surface-adsorbed, and surface-epitaxial particles. For example, the saturation behavior of the nucleation field at low Co content predicted by the simple curling model[17] for surface-coated particles, is found by us to be mainly due to neglect of the contribution of shell surface anisotropy. Here we present only the application of the present theory to cobalt-modified γ-Fe_2O_3 particles, and find satisfactory agreement between experiment and theory. However, this theory can be extended to investigate nucleation problems for other kinds of heterostructure particles, e.g., passivated iron particles,[30] particles coated with barium ferrite,[36] surfactant surface-chemisorbed particles,[37] etc.

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