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Simulating the Magnetization of an Ensemble of Cobalt-Coated γ-Fe₂O₃ Particles

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Abstract—In terms of a previously suggested model, magnetization of an ensemble of Co-coated γ-Fe₂O₃ particles is investigated. Thermal fluctuations and interphase interaction can substantially change the dependence of the coercive force on the geometric and structural characteristics of grains.

1. INTRODUCTION

The great interest in materials that are used in magnetic carriers refers entirely to materials consisting of ensembles of heterogeneous particles. Experimental studies of combinations of elements of the main and surface phases most suitable for magnetic recording were carried out on materials consisting, e.g., of γ-Fe₂O₃ particles coated with cobalt [1, 2], or molybdenum [3]; iron [4] or cobalt [5, 6] particles coated with native oxides; etc.

Experimental studies of such materials captured the interest of many theorists. Thus, Stavn and Morrish [7] generalized the model of a homogeneous particle [8] by considering the magnetization of ellipsoidal iron particles coated with γ-Fe₂O₃. Yang and Chang [9] refined the model of two-component particles [7] by allowing for interphase exchange interaction. Later on, the model of two-component particles was developed by discarding the requirement of magnetization uniformity in the bulk of grains. The problem of the magnetic-moment distribution in a two-component grain was solved by linearizing the equations of micromagnetism, which proved to be possible for only infinitely elongated cylindrical particles [10–12], or by using methods such as three-dimensional simulation [13] or minimization of the functional for a class of given functions [14, 15].

In our opinion, a substantial disadvantage of existing models is the assumption of the insignificance of the effect of thermal fluctuations on the grain magnetizations, although the sizes of particles used in the materials for magnetic recording are sufficiently small that the particles could be considered to be single-domain. For example, Co-coated γ-Fe₂O₃ particles have a diameter of about 40 nm, which is comparable with the characteristic size a_T at which thermal fluctuations exert a significant influence on the process of magnetization. Indeed, the probability for a transfer of the magnetic moment of a grain from one state into another is $W \approx f_0 \exp[-\Delta E/(k_B T)]$, where $\Delta E = H_c I_s a^3$ is the height of the potential barrier; H_c is the coercive force; I_s is the spontaneous magnetization; a is the particle size; and $f_0 \sim 10^{10}$ s⁻¹ is the frequency factor. Assuming $H_c \sim 2K/I_s$ (e.g., the magnetocrystalline anisotropy constant for γ-Fe₂O₃ is $K = 4.6 \times 10^4$ erg/cm³), we may estimate a_T as

$$a_T = \left\{ \ln\left(\frac{f_0}{W}\right) \frac{k_B T}{2K} \right\}^{1/3}. \quad (1)$$

For a sufficiently wide range of "lifetimes" of grain magnetizations in one of the states $\tau \sim 1/W \sim 1\text{--}10^{10}$ s, we obtain $a_T \sim 20\text{--}30$ nm. This range of a_T variation is determined in reality by the total anisotropy, which consists of the shape, magnetocrystalline, and exchange contributions.

We believe that by using the modified model developed in [16], we can estimate the effects of thermal fluctuations and interphase interaction on the hysteretic properties of cobalt-coated γ-Fe₂O₃ particles.

2. STATIC MAGNETIC STATES OF HETEROGENEOUS PARTICLES

Similar to [16], we assume that a two-phase particle is a parallelepiped with a base a^2 and a height qa, separated by a flat boundary into two ferromagnetic phases with relative volumes $1 - \varepsilon$ and ε, spontaneous magnetizations I_{s1} and I_{s2}, and dimensionless uniaxial anisotropy constants $k_1 = K_1/I_{s1}^2$ and $k_2 = K_2/I_{s2}^2$, respectively. We discard the limitation of the model of [16] related to the neglect of interphase exchange interaction. According to [9], the energy of interfacial exchange can be written as

$$E_{ex} = -\frac{2A_{in}}{\delta a} \cos(\theta_1 - \theta_2) qa^3, \quad (2)$$

where A_{in} is the interfacial exchange constant; δ is the width of a transition region (on the order of the lattice

<center>12</center>

parameter); and θ_1 and θ_2 are the angles between the magnetization vectors $\mathbf{I}_{s1}$ and $\mathbf{I}_{s2}$ of the phases and the long edge of the particle qa, respectively.

The free energy F of a grain placed in an external magnetic field H at zero temperature $(T = 0)$ can be written as the sum

$$F = E_a + E_m + E_{ex} + E_H, \qquad (3)$$

where the energy of magnetocrystalline anisotropy E_a, magnetostatic energy E_m, and the magnetic moment energy in an external field E_H were defined in [16, equations (1)–(3)].

Minimizing free energy (3) with respect to the angles θ_1 and θ_2 yields the set of equations

$$a_1 \cos\theta_1 \sin\theta_1 + N_{12}^* j \cos\theta_1 \sin\theta_2$$

$$- N_{21}^* j \cos\theta_2 \sin\theta_1 + \frac{H}{I_{s1}}(1-\varepsilon)\sin\theta_1 = 0;$$

$$\qquad (4)$$

$$a_2 j \cos\theta_2 \sin\theta_2 + N_{12}^* \cos\theta_2 \sin\theta_1$$

$$- N_{21}^* \cos\theta_1 \sin\theta_2 + \frac{H}{I_{s1}}\varepsilon \sin\theta_2 = 0;$$

where $a_1 = 2N_{11} + k_1(1-\varepsilon)$; $a_2 = 2N_{22} + k_2\varepsilon$; $j = I_{s2}/I_{s1}$; $N_{12}^* = N_{12} - A^*$; $N_{21}^* = N_{21} - A^*$; $A^* = \dfrac{2A_{in}}{\delta a I_{s1} I_{s2}}$; and N_{ik} are the demagnetizing factors.

An analysis of the set of equations (4) shows that at $H = 0$ the particles, as in the absence of interfacial exchange, can reside in one of the following four states:

1. $\theta_1 = 0$, $\theta_2 = 0$; 2. $\theta_1 = 0$, $\theta_2 = \pi$; 3. $\theta_1 = \pi$, $\theta_2 = \pi$; 4. $\theta_1 = \pi$, $\theta_2 = 0$.

Depending on the relationship between the energies of interfacial magnetostatic and exchange interactions, states with either parallel or antiparallel orientations of the magnetizations of the phases can be metastable. If the magnetostatic interaction dominates the exchange coupling ($N_{21}^* > 0$), then the first and third states are metastable, because the free energy $F = N_{21}^* I_{s1} I_{s2} qa^3$ of a grain in these states is greater than in the second or fourth states, where $F = -N_{21}^* I_{s1} I_{s2} qa^3$. If $N_{21}^* < 0$, then the second and fourth states are metastable.

In an external magnetic field $\mathbf{H}$, the magnetic states of particles can change. These changes are only possible if certain critical fields are attained, whose spectrum coincides with that studied in detail in [16]. The expressions for these critical fields only differ in the replacement of the demagnetizing factors N_{12} and N_{21} by N_{12}^* and N_{21}^*, respectively, which include the interfacial exchange constant A_{in}. For example, the critical field for the transition from the first state into the fourth state
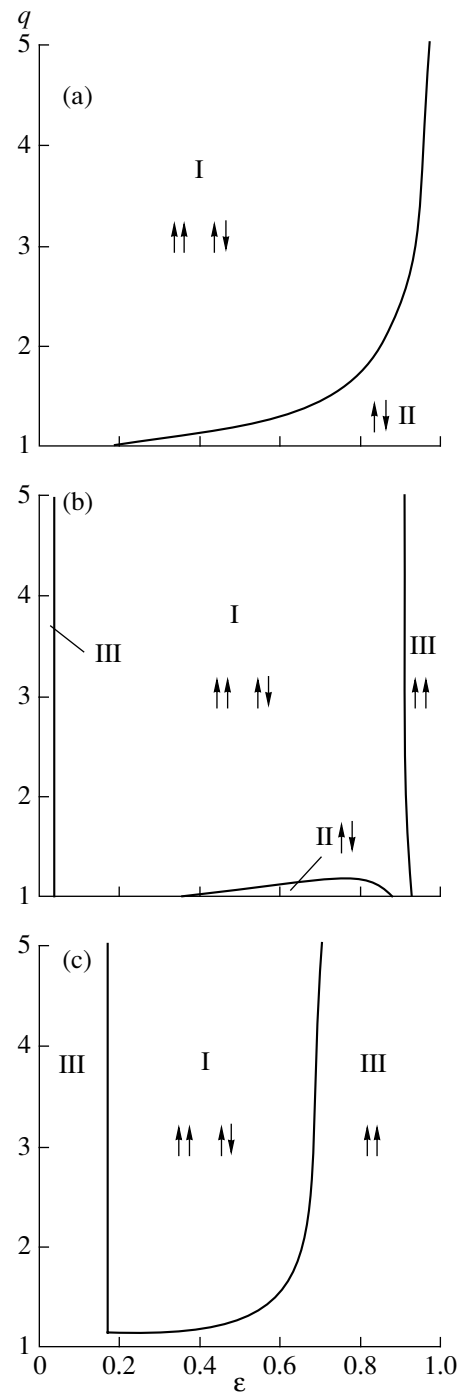

Fig. 1. Magnetic phase diagrams $\{\varepsilon, q\}$ of a system of cobalt-coated γ-Fe$_2$O$_3$ particles ($I_{s1} = I_{s2} = 350$ G, $k_1 = 0.38$, $k_2 = 4.08$): (a) $A^* = 0$, (b) $A^* = 0.2$, and (c) $A^* = 1$. Particles whose representative points lie in region I can be in one of four states (see text); regions II and III correspond to particles whose magnetic moments are oriented only either parallel or antiparallel to one another, respectively.

is defined by the following relation:

$$H_{c1}^{(\uparrow\uparrow)} = k_1 I_{s1} + \frac{2N_{11} I_{s1} - N_{21}^* I_{s2}}{1 - \varepsilon}, \qquad (5)$$
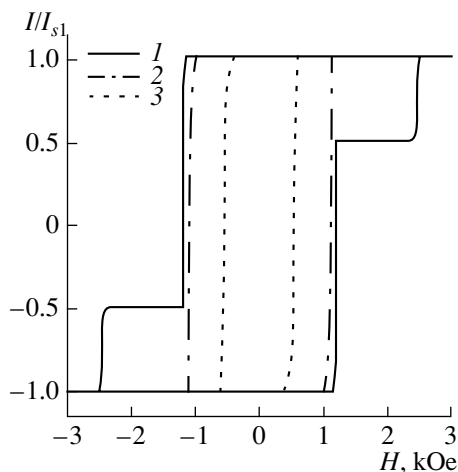
Fig. 2. Hysteresis loops for an ensemble of Co-coated γ-Fe$_2$O$_3$ particles ($q = 1.5$; $T_l = 2 \times 10^3$ s; $H_{max} = 10^4$ Oe; $A_{in} = 4.09 \times 10^{-8}$ erg/cm; $\delta = 8.35 \times 10^{-8}$ cm; $k_2 = 16.3$; and $\varepsilon = 0.25$): (*1*) $a = 40$; (*2*) 20; and (*3*) 15 nm.
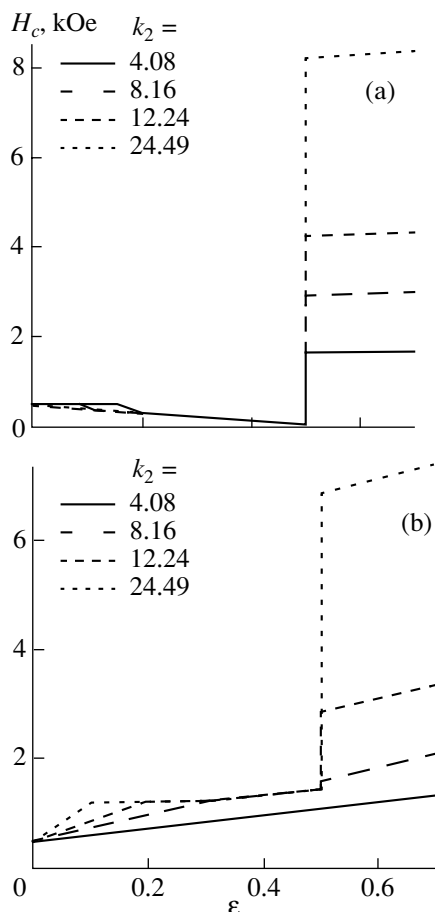

Fig. 3. Variation of the coercive force H_c as a function of the relative volume of the CoFe$_2$O$_4$ phase at various values of the anisotropy constant k_2 ($a = 40$ nm; $q = 1.5$; $T_l = 2 \times 10^3$ s; $H_{max} = 10^4$ Oe): (a) $A^* = 0$; and (b) $A^* = 2$.

which coincides with that obtained in [16] to within the re-defined factor N_{21}.

Phase diagrams shown in Fig. 1 illustrate the effect of interfacial exchange on the stability on the magnetic states of two-phase particles. An increase in the interfacial exchange to $A^* = 0.2$ leads to reorientation transitions from states with an antiparallel orientation into those with a parallel orientation of the magnetic moments of the phases (region III in Fig. 1b). A further increase in the interfacial exchange ($A^* = 1$) results in transitions into states with a parallel directions of the magnetizations of the phases at the expense of the antiparallel configurations.

3. MAGNETIZATION OF AN ENSEMBLE OF TWO-PHASE PARTICLES

Let us consider an ensemble of small (15–80 nm) Co-coated γ-Fe$_2$O$_3$ particles. According to [11, 13], the coating on such particles is cobalt ferrite. The composition of this ferrite is most likely to be close to CoFe$_2$O$_4$, whose spontaneous magnetization I_{s2} is assumed to be equal to the magnetization of γ-Fe$_2$O$_3$ ($I_{s1} = 350$ G). The magnetocrystalline anisotropy constant K_2 of CoFe$_2$O$_4$ was taken in the range $(0.5–3) \times 10^6$ erg/cm^3 [2, 9, 17]; this is much higher than that for γ-Fe$_2$O$_3$, for which $K_1 = 4.6 \times 10^4$ erg/cm^3. The value of the exchange constant A_{in} estimated theoretically [9] was 5.87×10^{-8} erg/cm. The frequency factor f_0 was assumed to be 10^{10} s^{-1}. The magnetostatic interaction was neglected.

Figures 3–7 display the dependences of the coercive force H_c on various characteristics of the particles calculated by simulating hysteresis loops (Fig. 2) in terms of the previously developed model of an ensemble of two-phase particles [16].

The behavior of the coercive force H_c depending on the volume fraction ε of the cobalt ferrite is mainly determined by the interfacial exchange. At $A^* = 0$, the coercive force of particles first decreases with increasing ε but then levels off (Figs. 3a, 4); at $A^* > 1.5$ H_c increases at any ε (Figs. 3b, 4). In addition, the exchange interaction somewhat decreases the maximum value of H_c, which increases with increasing magnetocrystalline anisotropy constant k_2 of the cobalt ferrite.

Such a dependence of H_c on ε can be explained as follows: so long as the magnetostatic interaction between phases prevails over the exchange interaction, the coercive force is determined by the minimum critical field $H_{c1}^{(\uparrow\uparrow)}$ which decreases with increasing the amount of the second phase. If the exchange interaction is prevailing ($A^* > N_{21}$), the phases undergo magnetization reversal coherently (curve *4* in Fig. 4 has no breaks). The exchange interaction increases the critical field $H_{c1}^{(\uparrow\uparrow)}$ and has no effect on the field $H_{c3}^{(\uparrow\uparrow)}$ of the
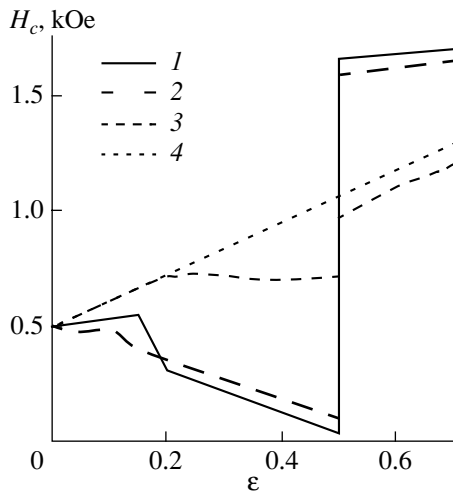
Fig. 4. Variation of the coercive force H_c as a function of the relative volume of the $CoFe_2O_4$ phase at various values of the anisotropy constant A^* ($a = 40$ nm; $q = 1.5$; $T_l = 2 \times 10^3$ s; $H_{max} = 10^4$ Oe; $k_2 = 4.08$): (*1*) $A^* = 0$; (*2*) $A^* = 0.1$; (*3*) $A^* = 1$; and (*4*) $A^* > 1.5$.
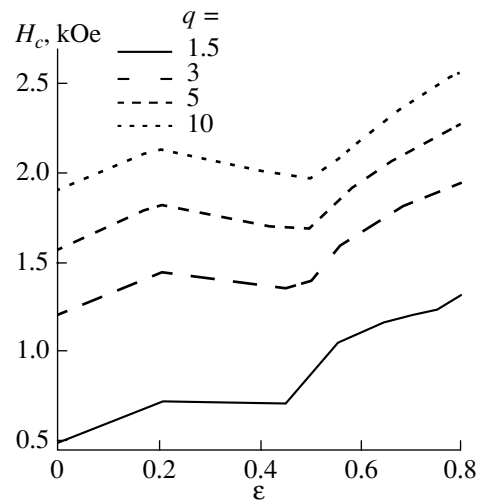

Fig. 5. Variation of the coercive force H_c as a function of the relative volume of the $CoFe_2O_4$ phase at various values of the oblongness q of particles ($a = 40$ nm; $T_l = 10^3$ s; $H_{max} = 10^4$ Oe; $A^* = 1$; and $k_2 = 4.08$).
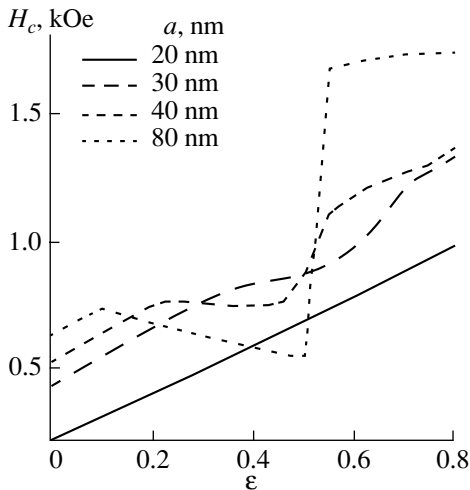

Fig. 6. Variation of the coercive force H_c as a function of the relative volume of the $CoFe_2O_4$ phase at various values of the particle size a ($q = 1.5$, $T_l = 1$ s, $H_{max} = 10^4$ Oe; $k_2 = 4.08$; $A_{in} = 2.05 \times 10^{-8}$ erg/cm; and $\delta = 8.35 \times 10^{-8}$ cm).
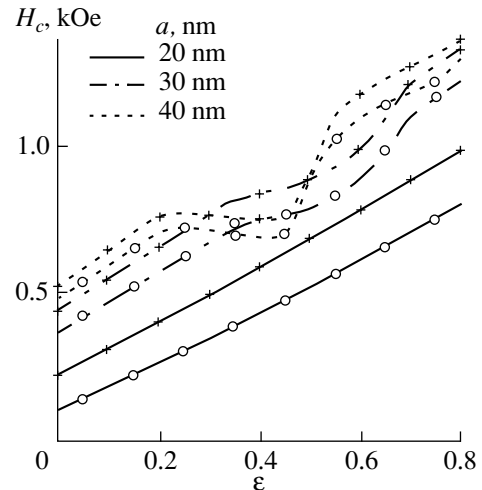

Fig. 7. Variation of the coercive force H_c as a function of the relative volume of the $CoFe_2O_4$ phase at various values of the period of the field variation T_l ($q = 1.5$; $H_{max} = 10^4$ Oe; $k_2 = 4.08$; $A_{in} = 2.05 \times 10^{-8}$ erg/cm; $\delta = 8.35 \times 10^{-8}$ cm): (+) $T_l = 1$ s; and (⊙) $T_l = 10^4$ s.

coherent magnetization reversal of a particle. The decrease in H_c noted above was not observed in [7, 9]; this is explained by the symmetric arrangement of the phases, in which case no interfacial exchange arises.

Note that at $\varepsilon > 0.5$, the coercive force of particles with an interfacial exchange constant $A^* = 1$ is less than that of particles with $A^* > 1.5$ (see curves *3* and *4* in Fig. 4). This is caused by the difference in the mechanisms of magnetization reversal of the phases: in the first case, the magnetic moments of the phases change their directions synchronously and by overcoming

potential barriers E_{13} and E_{31} (see [16]), the particle passes from state 1 into state 3, whereas in the second case, both coherent and independent switching is possible.

Figure 5 illustrates the effect of the grain oblongness on its coercive force. At large q, the calculated coercive forces differ from the experimental values, which can be related to the violation of the assumption on the uniform reversal of the magnetic moment of a grain.

A natural limitation for grain refinement in materials used for magnetic recording is related to the insta-

bility of remanent magnetization. Thermal fluctuations, whose role increases with decreasing grain size, lead to decreasing H_c (Fig. 6). The same conclusion follows from a comparison of critical fields (which correspond to transitions from one to another state) with the coercive force. For example, for particles with $a = 40$ nm, we have $H_c = 1.2$ kOe and the critical field $H_{c1}^{(\uparrow\uparrow)} = 1.4$ kOe; for the ensemble of particles with $a = 20$ nm, the coercive force is $H_c = 1.1$ kOe and the critical field is $H_{c3}^{(\uparrow\uparrow)} = 2.1$ kOe (see Fig. 2).

The process of magnetization reversal can be affected by relaxation phenomena. Thus, an increase in the magnetization (demagnetization) time T_l is seen to decrease H_c (Fig. 7).

A qualitative comparison of our calculated results with those presented in [9, 11, 12] indicates that, similar to those works, the coercive force increases to saturation with increasing volume fraction of the $CoFe_2O_4$ phase. In [9, 11, 12]], the saturation level was mainly determined by the magnitude of the exchange interaction constant, whereas the anisotropy constant K_2 mainly affects the initial slope of the H_c vs. R_2/R_1 curve, where R_2 and R_1 are the radii of cylindrical surfaces that bound the phases. This curve is monotone (in [9], this is the case only for large A), and the H_c dependence on the difference $1 - (B_1/B_2)^3$ [9] or $1 - (R_1/R_2)^2$ [11, 12], which is a countertype to ε, is nonlinear. In our calculations, the saturation level depends mainly on the anisotropy constant of cobalt ferrite, whereas the interfacial exchange mainly determines the shape of the $H_c(\varepsilon)$ curve. At small values of A^*, the $H_c(\varepsilon)$ curve is nonmonotonic, which is related to the adopted mutual arrangement of the phases.

CONCLUSIONS

(1) Effects of the exchange interaction between phases on the magnetic states of cobalt-coated γ-Fe_2O_3 particles were studied.

(2) The dependence of the coercive force of a system of small γ-Fe_2O_3 on the relative volume occupied by the cobalt coating particles was shown to be substantially affected by the relationship between the interfacial magnetostatic and exchange interactions.

(3) An increase in the magnetocrystalline anisotropy of the cobalt coating increases the coercive force of the ensemble of γ-Fe_2O_3 particles.

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