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Negative remanent magnetization of fine particles with competing cubic and uniaxial anisotropies

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The magnetic properties of noninteracting single-domain particles whose anisotropy is made up of a cubic magnetocrystalline and a uniaxial components were investigated. Various directions of the uniaxial anisotropy were considered and the dependencies of the reduced remanence as a function of the ratio between the two anisotropies were obtained. It was found that for sufficiently strong uniaxial anisotropy and random arrangement of the particle orientations, reduced remanence lower than 0.5 is, in general, an *intrinsic* property of the system due to the negative remanent magnetization of some of the particles. © *1998 American Institute of Physics.* [S0021-8979(98)03715-3]

I. INTRODUCTION

Fine-particle systems have attracted much attention recently[1–4] because of the wide range of their potential applications. Among them are magnetic recording (at present, nanostructured materials dominate in both information storage media and in the ''write'' and ''read'' heads), ferrofluids, catalysts, medical diagnostics, drug-delivery systems, color imaging, and pigments in paints and ceramics.

The problem of the hysteresis behavior of fine particles has been subject to considerable interest over many years. The first systematic calculations of magnetization were performed on uniaxial single-domain particle systems at zero temperature in 1948 by Stoner and Wohlfarth,[5] and for materials with cubic magnetocrystalline anisotropy in 1974 by Joffe and Heuberger.[6] The predicted remanent magnetization, M_r, for a random assembly of such multiaxial particles is equal to 0.831 and 0.866 M_s (M_s is the saturation magnetization) for positive and negative first-order magnetocrystalline anisotropy constant, K_1, respectively,[7] higher than the value of 0.5 M_s for uniaxial anisotropy. However, to date only one experimental evidence has been reported in the literature regarding the existence of multiaxial anisotropy in ultrafine particles, i.e., $M_r \geqslant 0.8\ M_s$.[8] Smaller values of M_r/M_s for such systems are normally attributed to elongation of the particles, stress, interparticle interactions, or thermal activation effects.

Some theoretical results were obtained for the remanent magnetization of single-domain particles having mixed uniaxial anisotropies by Wohlfarth and Tonge,[9] and some cases of particles with mixed uniaxial and cubic anisotropies were considered as well.[10] This situation arises, e.g., in iron or fcc cobalt particles having additional shape or strain anisotropy. Ultrathin films also provide conditions where uniaxial and cubic anisotropies coexist.

When there are competing anisotropies, new phenomena are seen. One of these is negative remanence. Some examples of this interesting behavior are given by Arrott[11] for several particular cases when a uniaxial (two-fold) anisotropy is superimposed upon a four-fold anisotropy.

In the present work, we report results on the remanence of fine-particle systems, when uniaxial and cubic anisotropies coexist. Both cases of positive and negative first-order cubic magnetocrystalline anisotropy constant have been considered.

II. COMPUTATIONAL PROCEDURE

Let us consider a system consisting of noninteracting single-domain particles whose anisotropy is made up of a cubic magnetocrystalline and an uniaxial components. Let the direction cosines of the magnetization vector $\mathbf{M}_s$ of such a particle are α_1, α_2 and α_3 and those of the uniaxial anisotropy l, m and n, referred to the cube axes. For fixed magnitude and direction of the applied field $\mathbf{H}$, neglecting the thermal activation effects and considering only coherent rotation of the magnetization, the total reduced free energy of the particle can be written as

$$\eta(\gamma,\vartheta)=\frac{E}{2|K_1|V}=\frac{1}{2}\text{sign}(K_1)(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)-\frac{K_u}{2|K_1|}(\alpha_1 l+\alpha_2 m+\alpha_3 n)^2-h\cos\phi, \tag{1}$$

where h is the reduced magnetic field $(=HM_s/2|K_1|)$, E the total energy, V the particle volume, K_u the uniaxial anisotropy constant which is here taken to be positive (negative values will be considered in another work), and $\cos\phi$ is given by

$$\cos\phi=\cos\gamma\cos\theta+\sin\gamma\sin\theta\cos(\vartheta-\psi). \tag{2}$$

Here γ and ϑ are the spherical coordinates of $\mathbf{M}_s$ and θ and ψ are those of $\mathbf{H}$; ϕ is the angle between $\mathbf{M}_s$ and $\mathbf{H}$.

In zero applied field, when $K_1>0$ and $K_u=0$ there are six minima of η along $\langle 100\rangle$ directions, and when $K_1<0$,

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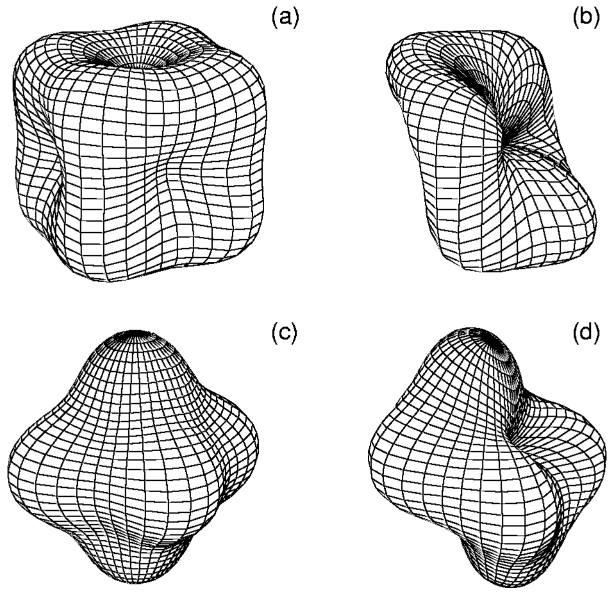

FIG. 1. Perspective drawings of zero field energy surface for direction of the uniaxial anisotropy along [111]: (a) $K_1>0$ and $K_u=0$; (b) $K_1>0$ and $K_u/K_1=0.6$; (c) $K_1<0$ and $K_u=0$; and (d) $K_1<0$ and $K_u/|K_1|=0.6$.

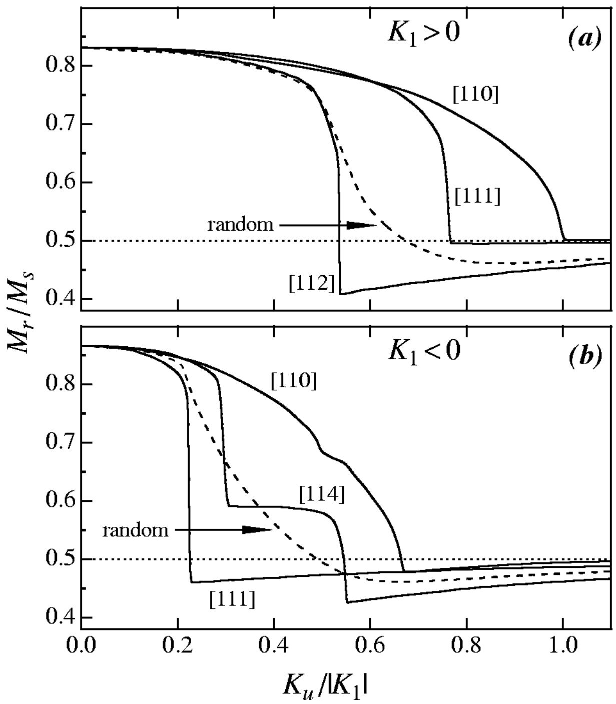

FIG. 2. M_r/M_s vs $K_u/|K_1|$ for different $[l,m,n]$; (a) positive K_1 and (b) negative K_1; The dashed curves are for systems with random directions of the uniaxial anisotropy.

there are eight easy directions of $\langle 111\rangle$ type. As $K_u/|K_1|$ increases, these minima move towards the direction $[l,m,n]$ and, in general, they reach this direction only when $K_u/|K_1|\rightarrow\infty$. Figure 1 shows the energy surface at zero field for some representative cases. One should note that the energy symmetry is lowered when a nonzero uniaxial anisotropy term is introduced in the energy expression; this property will be essentially used in the next section to explain the negative remanence of some particles.

When $h\neq 0$, the energy function can only be minimized numerically. If the sample is saturated in a large positive field, only one position of (γ,ϑ) is stable and located in the first octant. However, as h becomes negative, this energy minimum is raised, the equilibrium becomes metastable and, with increasing reverse field, unstable. The magnetization will swing out of the first octant, and it is here that a systematic approach must be introduced to determine the path leading to the relevant local minimum. The computer model used in the present work is the one developed in Refs. 12 and 13, as the two-variable minimization procedure was modified in order to make the search of minima more efficient in regions where the energy changes rapidly. If, e.g., the starting reference point is near to a maximum and the initial step length is sufficiently large, the maximum can be overcome and the algorithm may find a minimum, which is not the one closest to the starting point. In order to solve this possible problem, before the two-variable minimization algorithm is started, each of γ and ϑ is fixed and the nearest minimum of $-\eta$ for the other variable is found, i.e., the nearest maximum or saddle point of η is found. If the initial step of the corresponding variable is too large, this step is decreased so the maximum of η is not to be overcome, and then the main two-variable minimization is initiated.

III. RESULTS AND DISCUSSION

Using the above procedure, demagnetization curves (h decreasing from a large positive value to 0) for a random assembly of single-domain particles with competing uniaxial and cubic anisotropy are obtained scanning over the uniaxial anisotropy directions given by $[l,m,n]$. This process was carried out for the spherical angles of $[l,m,n]$ both changed in increments of $\pi/150$ so the points of intersection of these directions with a sphere form an isosceles right-angled spherical triangle, which represents a 48th part of a sphere of all directions, which contains all physically different directions in a cubic lattice. Such a spherical triangle is the one formed by the points of intersections of [001], [101], and [111] with a sphere.

The dependencies of M_r/M_s on $[l,m,n]$ direction were calculated for various values of $K_u/|K_1|$. When $K_u/|K_1|=1$, the uniaxial anisotropy dominates over the cubic one for all $[l,m,n]$, so the number of minimum energy directions is reduced to 2. However, M_r/M_s is equal or *less* than 0.5. Actually, there are only three $[l,m,n]$ directions for which $M_r/M_s=0.5$: the $\langle 100\rangle$ or $\langle 110\rangle$ for $K_1>0$, and $\langle 110\rangle$ for $K_1<0$. For all other cases, $M_r/M_s<0.5$ and reaches 0.5 only when $K_u/|K_1|\rightarrow\infty$.

Tonge and Wohlfarth[10] calculated the dependence of M_r/M_s on $K_u/|K_1|$ for $[l,m,n]$ given by [100] direction only. Our method allows calculations of the magnetization and the remanence for any $[l,m,n]$ direction. Figure 2 shows M_r/M_s vs $K_u/|K_1|$ for several representative $[l,m,n]$ directions. It can be seen that M_r/M_s can reach values rather lower than 0.5, e.g., when $[l,m,n]$ is given by [112] direction, $K_1>0$, and $K_u/K_1=0.54$, then $M_r/M_s=0.4$.

TABLE I. Values of the critical aspect ratio p_{crit}, for which $M_r/M_s = 0.5$ for several materials with cubic magnetocrystalline anisotropy and $|K_1| < M_s^2$ at room temperature, and $K_u^{max}/|K_1|$ for materials with $|K_1| \gg M_s^2$.

Materials with $|K_1| < M_s^2$	p_{crit} ($M_r/M_s = 0.5$)	Materials with $|K_1| \gg M_s^2$	$K_u^{max}/|K_1|$
Fe	1.045	$CoFe_2O_4$ (4.2 K)	0.04
Ni	1.04	$TbFe_2$ (300 K)	0.03
fcc Co	1.12	$DyFe_2$ (300 K)	0.05
Fe_3O_4	1.06	$HoFe_2$ (300 K)	0.09
γ-Fe_2O_3	1.08	$ErFe_2$ (300 K)	0.07
$MnFe_2O_4$	1.04	$TbAl_2$ (4.2 K)	0.08

The dashed curves in Figs. 2(a) and 2(b) refer to one more general case. Besides of the random (in respect to the **H** direction) particle orientations, random $[l,m,n]$ directions are also allowed. Our calculations give that $M_r/M_s \leqslant 0.5$ for $K_u/K_1 \geqslant 0.67$ (when $K_1 > 0$) and $K_u/|K_1| \geqslant 0.49$ ($K_1 < 0$). If the uniaxial anisotropy comes from the shape (elongation) of the particles, the form $K_u = \frac{1}{2}(N_a - N_c)M_s^2$ is used for prolate spheroid (an ellipsoid for which two axes are equal, say $a = b$, $c > a$, and $N_a = N_b$), where N_a, N_b and N_c are the demagnetization factors along the principal axes of the spheroid. Using the above critical values from the dashed curves and the equations of Osborn[14]

$$N_c = \frac{4\pi}{p^2 - 1}\left[\frac{1}{2\xi}\ln\left(\frac{1+\xi}{1-\xi}\right) - 1\right], \tag{3}$$

$$N_a = 2\pi - \frac{1}{2}N_c \tag{4}$$

[where $p = c/a$ (>1) and $\xi = \sqrt{p^2 - 1}/p$], as well as the values of M_s and K_1 for any particular material, one can obtain the critical value of the aspect ratio, p_{crit}, above which the uniaxial anisotropy dominates for a disordered system with random $[l,m,n]$ directions for this material.

The values of p_{crit} for several materials are given in Table I. It is seen, that for materials with $|K_1| < M_s^2$, only slight particle elongation ($p < 1.1$) leads to remanence less than 0.5. It explains why there are no reported experimental data in the literature regarding the existence of such fine-particle systems (for which $|K_1| < M_s^2$) with high remanence, even at 4.2 K. Even for $[l,m,n]$ given by [100] and $K_u/|K_1| = 1$ so that $M_r/M_s = 0.5$, the corresponding aspect ratios are $p = 1.07$ for Fe and $p = 1.08$ for Ni.

Let us now consider the case when $|K_1| > M_s^2$. The maximum value of K_u is obtained for greatly elongated particles, ($N_c \ll N_a$), when $N_a - N_c \approx 2\pi$, so $K_u^{max} \approx \pi M_s^2$. For cobalt ferrite[8] ($M_s = 135$ emu/cm^3 and $K_1 = 1.6 \times 10^7$ erg/cm^3), we have $K_u^{max}/K_1 = 0.04$, which means that the cubic anisotropy always dominates over the shape one and the remanence will be high in the absence of thermal activation effects [see Fig. 2(a)]. The last result is supported by the data of Davies *et al.*,[8] having $M_r/M_s = 0.8$ for their ultrafine cobalt ferrite particles at 4.2 K, and those of Grigorova *et al.*[15] ($M_r/M_s = 0.64$ for $H^{max} = 50$ kOe at 5 K). The same calculations for $TbFe_2$ give low maximum uniaxial anisotropy as well, $K_u^{max}/|K_1| = 0.03$ at room temperature from the dashed curve in Fig. 2(b), and 0.006 at 4.2 K,[16] thus explaining the relatively high experimental reduced remanence of 0.6 at 77 K.[17] Therefore, for materials with $|K_1| \gg M_s^2$, the crystal anisotropy predominates and such fine-particle systems should have high remanent magnetization values in the absence of thermal activation effects. Values of $K_u^{max}/|K_1|$ for $CoFe_2O_4$ and for several Laves phase compounds are given in Table I.

Reduced remanence values lower than 0.5 for systems with competing cubic and uniaxial anisotropies come from the fact that some particles have *negative* remanent magnetization contribution, i.e., in the decreasing part of their hysteresis loops the magnetization becomes negative when the applied field is still positive. Such inverted hysteresis loops have been observed in a number of multilayer and thin film systems.[18–26] Attempts to relate this phenomenon either to interface exchange interaction[21–23] or to exchange anisotropy[27] have been made. Arrott[11] investigated some cases of negative remanence when a uniaxial (two-fold) anisotropy is superimposed upon a four-fold anisotropy. An example of inverted hysteresis loop for the case of a particle with competing anisotropies is demonstrated below.

Let us consider energy of the form as in Eq. (1) with negative K_1, $K_u/|K_1| = 0.6$, and $[l,m,n]$ given by [111]. The zero field energy surface for this case is shown in Fig. 1(d): the energy has two minima, $\gamma_1^{min} = \arccos 1/\sqrt{3} \simeq 55°$ and $\vartheta_1^{min} = 45°$, and the opposite direction. The hysteresis loop and dc demagnetization remanence curve,[28] M_d/M_s, for a particle with **H** applied in the (110) plane with $\theta = 150°$ are shown in Fig. 3. In this particular case, the magnetization rotates in the (110) plane only. The most interesting characteristics of this figure is the inverted hysteresis loop, i.e., in the low-field region the two branches of the loop are crossed, resulting in negative remanence and coercivity. This is due to the asymmetry of the zero field energy (see the largest inset in the figure): the point of the maximum is not equidistant from the two minima. As a result, if the saturation field is applied at an angle, higher than $\gamma_1^{min} + \pi/2$ but less than the angle of the maximum point (as it is the case in Fig. 3), after recoil the magnetization will relax in γ_1^{min}. The corresponding reduced remanence is $\cos(150° - 55°) < 0$.

Figure 4 shows the dependencies of M_r/M_s, and the reduced coercivity, h_c, on the polar angle of the field θ, when **H** is applied in the (110) plane for particles with negative K_1, $K_u/|K_1| = 0.6$ and $[l,m,n]$ along [111], as well as for $K_1 = 0$. [Here $h_c = H_c/(2|K_1|/M_s)$ for $K_1 \neq 0$, and $H_c/(2K_u/M_s)$ for Stoner–Wohlfarth particles when $K_1 = 0$]. It can be seen, that the area with negative remanent magnetization and coercivity is rather wide, even in the present case, which is not the extreme one. If, e.g., one has a granular film with particles as above, so that the (110) plane of each particle lies in the film plane, and random in-plane orientations are allowed, then $M_r/M_s = 0.43$. The closer (and higher) is $K_u/|K_1|$ to the corresponding critical value for the number of minimum energy directions to be reduced to 2, the larger is the number of particles with negative remanence, and the lower is M_r/M_s of the system.

In summary, the dependencies of M_r/M_s vs $K_u/|K_1|$ for

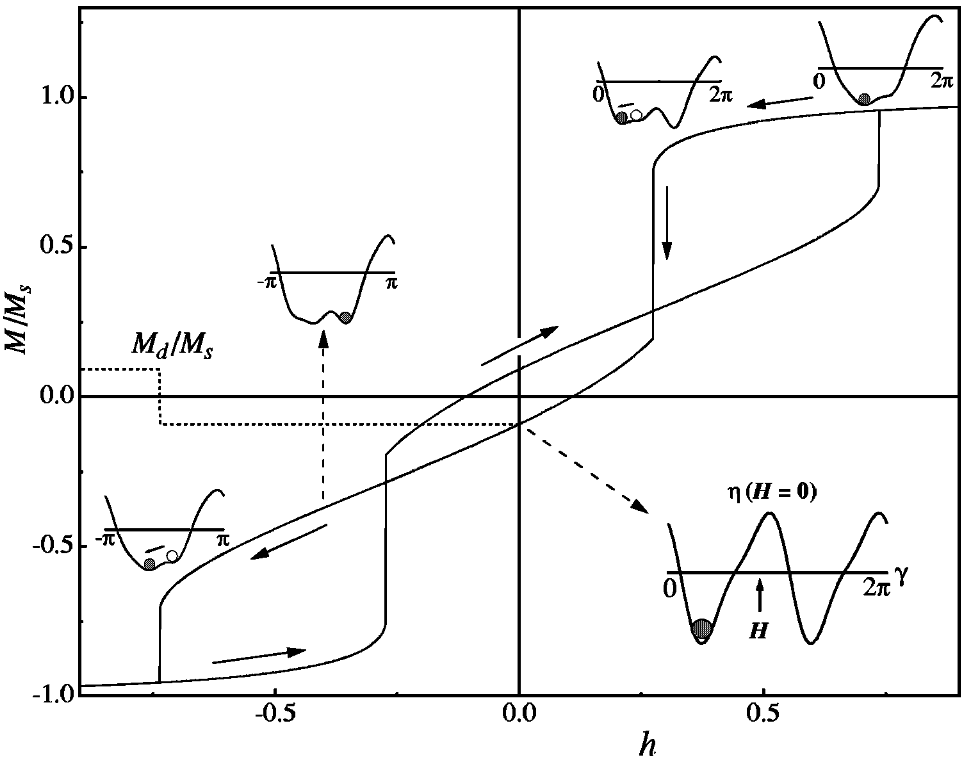

FIG. 3. Hysteresis loop and M_d/M_s curve for a particle with $K_1<0$, $K_u/|K_1|=0.6$, $[l,m,n]$ given by [111], and **H** direction given by $\theta=150°$ and $\psi=45°$. The solid arrows indicate the direction of the magnetization changes in the loop. The dependence of η on the angle γ for different values of the reduced field strength h in the (110) plane is shown for some cases as well. The position of the field with respect to the angle of the magnetization is indicated by the small upward arrow on the γ axis in the largest inset. The sequences of stable magnetization are found by following the positions of the closed circles. The transitions from metastable (open circles) to stable states are indicated for the two magnetization jumps in the loop.

different $[l,m,n]$ directions for systems consisting of noninteracting single-domain particles with competing cubic magnetocrystalline and uniaxial anisotropy components have been calculated. The case of random (in respect to the cube axes) directions of the uniaxial anisotropy has been considered as well. It was obtained that there are only three $[l,m,n]$ directions for which $M_r/M_s \geqslant 0.5$, and in general, for sufficiently strong uniaxial anisotropy and random arrangement of the particle orientations, $M_r/M_s<0.5$.

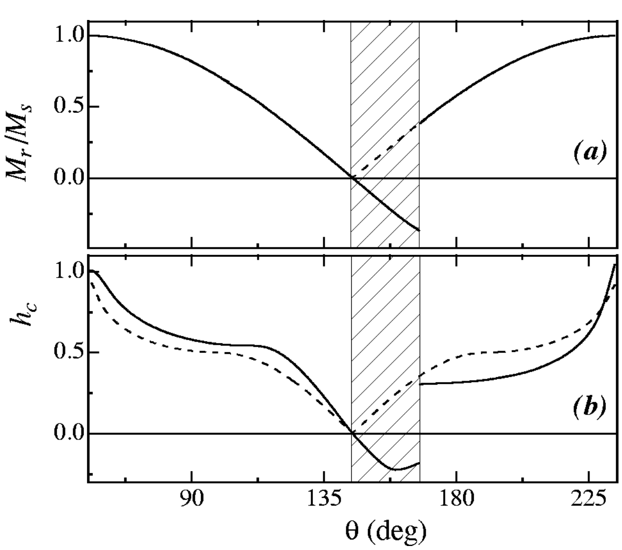

FIG. 4. M_r/M_s (a) and h_c (b) vs θ when **H** applied in the $(1\bar{1}0)$ plane for particles with negative K_1 and $K_u/|K_1|=0.6$ (solid lines), and $K_1=0$ (dashed lines). The $[l,m,n]$ direction is [111]. The shadowed area represents the orientations with negative remanence and coercivity.

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