Domain structure and magnetic properties of $YFeO_3$ particles below the single-domain critical size

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The possible existence of a multidomain structure in particles of dimensions smaller than the critical single-domain size is established by visual observation of the domain structures of single-crystal $YFeO_3$ particles. This structure is metastable and can be obtained during the course of thermal magnetization of the particles. It is shown that the existence of the metastable structure is due to the presence of an energy barrier that separates the multidomain state of the particle from the single-domain state.

1. The question of the domain structure (DS) and the magnetic properties of small particles, with dimensions smaller than the critical dimensions of single domains, has not yet been sufficiently investigated. As is well known[1] two critical dimensions, d_0 and d_c, are connected with the single-domain state. In particles with dimensions $d < d_0$, the single-domain structure is preserved during the course of particle magnetization-reversal that proceeds via uniform rotation of the spins. In the dimension range $d_0 < d < d_c$, the one-domain structure that is at equilibrium in the absence of a field may become destroyed if magnetization reversal is produced by some incoherent spin rotation.

Theoretical estimates show that in ordinary ferromagnets even the largest of the critical dimensions, d_c, does not exceed several microns. Consequently, investigations of the domain structure and the magnetic properties of the particles in the region where equilibrium single-domain states exist is a very complicated problem, which has remained practically unsolved to date.

Attractive prospects are afforded by the study of orthoferrites of rare-earth metals and yttrium. These substances pertain to the class of weak ferromagnets, with a resultant magnetic moment $I_s \sim 10$ G, a Curie temperature $T_c \sim 300-400°$ C, and a magnetic-anisotropy constant $K \sim 10^5$ erg/cm^2. In accordance with these characteristics, we obtained theoretical estimates for $d_c \sim 300\ \mu$ and $d_0 \sim 1\ \mu$. This leads to the possibility of visual detailed study of the domain structure and of the magnetization process using individual particles with dimensions on the order of d_c. The present paper deals with these questions.

2. We investigated single-crystal particles of yttrium orthoferrite with dimensions from 30 to 800 μ, grown by the method of spontaneous crystallization from the solution in the melt. All the particles had shapes close to parallelepipeds. The dimensions of some of the particles are listed in the table. The first two figures correspond to the dimension in the plane perpendicular to the easy-magnetization axis (the crystallographic axis c), and the last to the dimension along this axis.

Magnetic characteristics of certain single-crystal particles of yttrium orthoferrite

	A		B					C		
	1	2	3	4	5	6	7	8	9	10
Dimension, μ	650 850 1500	600 760 750	120 130 90	90 130 120	80 95 70	60 75 100	50 70 50	130 200 120	85 95 85	35 50 —
H_s, Oe	17	28	20	8	18	17	19	—	—	—
H_N, Oe	16	32	50	30	40	35	40	45	35	—
H_s/H_N	1.06	0.90	0.40	0.27	0.45	0.49	0.47	—	—	—
H_{c1}, Oe	270	100	1500	850	2500	1000	2600	820	6500	7500
H_c, Oe	550	500	1500	850	3600	3800	6200	2600	7100	7500

The domain structure was observed by the method of magnetic suspension, on particle natural faces perpendicular to the c axis. It should be noted that the shape of the cross section in the central part of the particle was more regular, close to rectangular, than the shape of the faces on which the domain structure was observed. The external magnetic field was oriented parallel to the c axis and was produced by a solenoid (up to 0.4 kOe) or by an electromagnet (up to 13 kOe). The particles were magnetized also by using a strong pulsed field (up to 140 kOe). The particles were demagnetized by heating above the Curie point (T_c = 375° C) and subsequent cooling in a magnetic screen (thermal demagnetization).

3. The observations of the domain structures of many of the particles, after multiple thermal demagnetization, have shown the following: Large particles with dimensions $d > 300\ \mu$ (group A) always had a multidomain structure, consisting of two or three domains (Fig. 1A). Among the smaller particles with $d < 300\ \mu$, some particles (group C) always had a one-domain structure (Fig. 1C), and in the other cases the form of the domain structure could not always be reproducible (group B), and the particle could have either one or two domains. A typical domain structure in the two-domain state for particles of this group is shown in Fig. 1B.

The observations have also shown that the probability of observing a particle after thermal demagnetization in the one-domain state is higher the smaller the particle dimension.

When the magnetic field is turned on, the magnetiza-

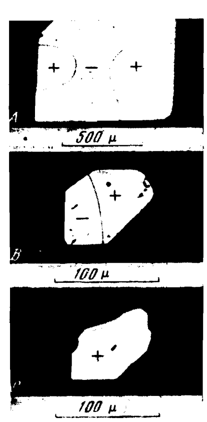

FIG. 1. Form of the domain structure on yttrium-orthoferrite natural faces perpendicular to the easy-magnetization axis: A—three-domain particle, B—two-domain particle, C-one-domain particle. The signs plus and minus indicate the direction of the magnetization in the domains.

tion of particles with multidomain structure proceeds via displacement of the domain walls. In particles of group B, the displacement process had a clearly pronounced jumplike character. Magnetic saturation was reached after several jumps of the wall, and sometimes only one jump. It should be particularly noted in this case that the saturation field H_S of the particles of this group was always noticeably weaker than their proper demagnetizing field $H_N = NI_S$, where N is the demagnetizing factor along the c axis, calculated for each particle on the basis of its dimensions in accordance with the formula introduced by Joseph [5]. In larger particles, however, saturation was reached as a rule in fields $H_S \approx H_N$.

The values of the fields H_S and H_N and the ratio H_S/H_N are given for some of the investigated particles in the table. For particles of group B, the ratio H_S/H_N was usually 0.3—0.5 (reaching ~0.1 in individual particles), whereas in particles of group A the value of this ratio was of the order of unity.

Regardless of the dimension, all the multidomain particles became single-domain after applying the field H_S. Their subsequent behavior in the field was identical to the behavior of particles with initial single-domain structure (Fig. 1c). This was manifest, first, in the fact that the particle magnetization reversal took place jumpwise in negative fields greatly exceeding the field H_S in absolute magnitude. Second, regardless of the initial domain structure, for some particles the coercive force H_{c1} corresponding to this jump was equal to the limiting coercive force H_c (these are particles 3, 4, and 10 in the table), while for others we had $H_{c1} < H_c$, i.e., in these particles the coercive force depends on the magnetizing field. This indicates that relatively stable ready-made magnetization-reversal nuclei can exist in the particles, including the one-dimensional particles after thermal demagnetization, and these nuclei are irreversibly annihilated by a sufficiently strong external field [6,7].

The measurements have shown, and this is in part reflected in the table, that the smaller the particle dimension the more probable are high values of H_{c1} and H_c. It was also noted that in small particles the dependence of the coercive force on the field is less pronounced or even nonexistent.

4. An analysis of the results suggests that in all particles with d < 300 μ the equilibrium structure is the one-domain structure, while the multidomain structure, as well as the presence of ready-made magnetization-reversal nuclei in certain one-domain particles, corresponds to metastable states. This assumption is based on the fact that a multidomain particle with dimension d < 300 μ, tending to an equilibrium state, becomes one-domain when a relatively weak field $H_S < H_N$ is turned on, whereas a field $H_S \approx H_N$ is needed to magnetize to saturation particles with dimensions d > 300 μ in which the multidomain structure is at equilibrium.

The appearance of metastable states in the particles can be explained in the following manner: In the immediate vicinity of the Curie point, the magnetic ordering sets in not uniform over the entire volume of the particle, but in individual regions. These regions can have oppositely directed magnetizations. Domain walls are produced during the course of the subsequent growth and "joining" of these regions. When the particle is subsequently cooled, these walls can remain in the particle, both as a result of their interaction with the crystal-structure defects, and because of the appearance, even in an ideal crystal, of energy barriers to the displacement of the domain wall. The latter situation is theoretically admissible in particles with dimension $d < d_c$.

Indeed, let us consider a spherical particle of radius R. Let the particle be divided by a domain wall of thickness $\delta \ll R$ into two domains with antiparallel magnetization orientation. The total energy of such a particle, comprising the domain-wall energy and the magnetostatic energy, is given by

$$F=\frac{3\gamma}{4R}V(1-t^2)+F_{\rm mst} \tag{1}$$

where

$$\gamma=4K\delta,\quad \delta=\left(\frac{A}{2K}\right)^{1/2},\quad t=\frac{x}{R}\leqslant 1,\quad V=\frac{4}{3}\pi R^3. \tag{2}$$

Here A is the exchange parameter, x is the displacement of the wall from the center of the particle, γ is the particle energy per unit particle surface, and V is the volume of the particle. The magnetostatic energy was calculated for this case by Neel [8] and is given by

$$F_{\rm mst}=4\pi^2 I_s^2 R^3\sum_{n=1}^{\infty}\frac{n(n+1)}{(2n+1)^2}C_n^2; \tag{3}$$

$$C_1=\frac{1}{5}(P_3-P_5),\quad C_n=\frac{P_{n-2}-P_n}{2n-1}-\frac{P_n-P_{n+2}}{2n+3},\quad n\geqslant 2, \tag{4}$$

where $P_n(t)$ are Legendre polynomials. It is seen from (3) that the magnetostatic energy F_{mst} is a series with increasing even powers of t:

$$F_{\rm mst}=4\pi^2 I_s^2 R^3\sum_{n=0} a_n t^{2n}, \tag{3'}$$

where a_n are the coefficients of the series.

It will now be more convenient to change to dimensionless quantities, referring the total particle energy F to the energy of a uniformly magnetized particle of the same radius: $F_0 = 2\pi I_S^2 V/3$. Then

$$\varepsilon\equiv\frac{F}{F_0}=\frac{r}{R}(1-t^2)+\frac{9}{2}\sum_{n=0}^{\infty}a_n t^{2n}, \tag{1'}$$

where

$$r=9\gamma/8\pi I_s^2. \tag{5}$$

The energy ϵ has a minimum at t = 0 and $R > R_1$, where

$$R_1=\frac{2r}{9a_1},\quad a_1=\frac{5}{16}-\sum_{n=2}^{\infty}\frac{(2n-1)(2n+1)}{2n+2}\left[\frac{(2n-3)!!}{2n!!}\right]^2\approx 0.213. \tag{6}$$

On the other hand, equating the total energy of the particle (1) to the energy of a uniformly magnetized particle, we obtain for the critical radius of the one-domain state

$$R_c=\frac{2r}{2-9a_0},\quad a_0=\frac{3}{32}+\sum_{n=2}^{\infty}2n(2n+1)\left[\frac{(2n-3)!!}{(2n+2)!!}\right]^2\approx 0.108. \tag{7}$$

Thus, at least in spherical particles, with dimensions in the interval

$$R_1<R<R_c, \tag{8}$$

or equivalently 0.514 < r/R < 0.959, metastable states can exist with the domain wall located at the center of the particle. Figure 2 shows by way of example the dependence of the magnetostatic energy ϵ_{mst} (curve 1), the domain-wall energy (curve 2), and the total energy ϵ (curve 3) on the wall-displacement parameter t at r/R = 0.6. We see that when the wall is located at the center of the particle, (t = 0), there is a relative minimum of the energy, separated from the absolute minimum ϵ = 1 (homogeneously magnetized state) by an energy barrier. This wall is in a position of stable equilibrium.

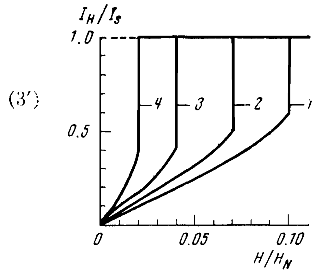

FIG. 3

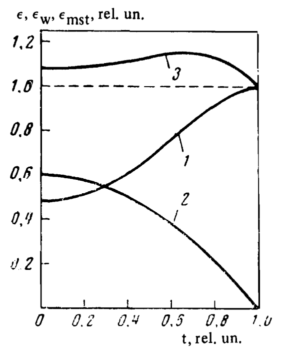

FIG. 2

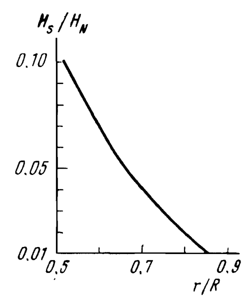

FIG. 4

FIG. 2. Dependence of the magnetostatic energy ϵ_{mst} (curve 1), of the domain-wall energy ϵ_W (curve 2), and of the total energy $\epsilon = \epsilon_{mst} + \epsilon_W$ (curve 3) on the wall position in a spherical particle at r/R = 0.6.

FIG. 3. Magnetization curves of two-domain particles for r/R values 0.52 (1), 0.6 (2), 0.7 (3), and 0.8 (4).

FIG. 4. Dependence of the saturation field on the dimension of the spherical particle.

When an external field H is applied along the easy magnetization axis of the crystal, the wall begins to move away from the position corresponding to t = 0. The equilibrium wall position t_H is determined in this case from the minimum of the sum of the energy ϵ and of the particle energy ϵ_H in the external field. In dimensionless units, the latter is given by

$$\varepsilon_H = -ht(3-t^2),\quad h = H/H_N,\quad H_N = \tfrac{4}{3}\pi I_s. \qquad (9)$$

The calculation of t_H was carried out by a numerical method, and the results were used to plot magnetization curves which in our case are described by the formula

$$I_H/I_s = \tfrac{1}{2} t_H (3 - t_H^2). \qquad (10)$$

Figure 3 shows the results of this calculation for four values of the parameter r/R from the indicated interval of variation of R. We note first that in the absence of a field the spherical particle is in the demagnetized state. When the field is increased from zero, the wall begins to move smoothly from the center of the particle to its edge. This leads to a gradual growth of the magnetization I_H at all the considered values of r/R. When a certain field H_S, which depends on the magnetic characteristics of the crystal and on the radius R, is reached, the stable position of the wall vanishes and the wall leaves the crystal jumpwise, leading to a jumplike growth of the magnetization to a value $I_H = I_S$. With subsequent decrease of the field H from the value $H > H_S$ to zero, the particle remains in the one-domain state. In this state, it has the lowest energy (Fig. 2).

It follows from the results that saturation of the particle is reached in the fields much weaker than the demagnetizing field H_N. The saturation field decreases with decreasing radius R. This relation is shown in Fig. 4.

For spherical yttrium-orthoferrite particles at $I_S = 9$ G, $K = 4.5 \times 10^5$ erg/cm^3 [9], and $A \sim 10^{-6}$ erg/cm ($\gamma \approx 2$ erg/cm^2) we have $d_1 = 2R_1 \approx 180\ \mu$, $d_c = 2R_c \approx 340\ \mu$, and $\delta \sim 100$ Å. We see therefore that $\delta/d_c < \delta/d_1 \ll 1$. Therefore the theoretical results obtained above are fully applicable to spherical particles of yttrium orthoferrites whose dimensions lie in the interval $180 < d < 340\ \mu$.

One can expect the laws governing the magnetic behavior of the particles with metastable domain structure to become even more clearly pronounced in particles of rectangular shape, inasmuch as at a constant area of the domain wall the height of the energy barrier that prevents the transition to the one-domain state is determined mainly by the magnetostatic energy of the particle.

Thus, the theoretical analysis shows that even in an ideal particle with dimension $d < d_c$ there can exist a metastable domain structure connected with a stable position of the domain wall.

In real particles, an important role in the formation of the metastable domain structure can be played by various types of defects due to imperfection in the shape and imperfection in the crystal structure of the particles. These defects can exert an influence on the growth of the magnetically ordered regions near T_c, and on the stability of the produced domain walls. Individual peculiarities of the particles can explain why some particles with $d < d_c$ have a one-domain structure after thermal demagnetization, while in others the one-domain structure is violated by the presence of ready-made nuclei of magnetization reversal, while still others are in a two-domain state. The appearance of a domain structure of one type or another is not strictly connected with the geometrical dimensions and the shape of the particle. The fact that the type of the domain structure is not reproducible in individual particles after repeated thermal demagnetization indicates that the process of domain-structure formation is sensitive to small accidental changes of the external conditions.

The pinning of domain walls on defects serves as an additional cause of their stability in particles with $d < d_c$. In the case when this pinning is not too strong, magnetic saturation, as in an ideal particle, will be reached in fields $H_S < H_n$, but the value of the field H_S itself will be larger than that theoretically expected. For a comparison of the values of H_S/H_N, listed in the table, with those calculated theoretically (Fig. 4), we can conclude that it is precisely this situation which is realized in yttrium orthoferrite particles.

It was noted above that with decreasing dimension the probability of observing the particle in a one-domain state increases. On the one hand, this can be attributed to the fact that in small particles the energy barrier that prevents the displacement of the domain wall is smaller, and consequently the probability of the onset of a two-domain state during the process of thermal demagnetization is smaller. On the other hand, one can assume that the number of defects in the particles is decreased and accordingly the conditions for the appearance of domain walls near T_c become worse, as do the conditions for the stabilization of their position following the subsequent cooling. The decrease in the number of defects in the particles can also be the reason why smaller particles have a higher coercive force and the dependence of the coercive force on the magnetizing field is less pronounced in them.

We note also that although in particles with $d < d_c$ it is the one-domain structure which is the equilibrium structure in the absence of the field, reversal of the magnetization of these particles along the limiting hysteresis loop occurs, in all probability, via growth of magnetization-reversal nuclei, which are produced in sections with decreased magnetic anisotropy. This is indicated by the relatively low values of the coercive force of the particles, in comparison with the anisotropy field $H_a \sim 10^5$ Oe.

Thus, from an analysis of both the theoretical and experimental results it follows that in particles whose dimensions are lower than the critical dimension d_c at which a one-domain structure occurs, there can exist metastable states with multidomain structures. These states can be obtained after thermal demagnetization of the particles. A particle with metastable structure can be magnetized to saturation in a field much weaker than its proper demagnetizing field. It is to be expected that the regularities of the domain structure and of the magnetic properties established through the study of single-crystal yttrium-orthoferrite particles, in the region of the transition from the multi-domain state to the one-domain state, will become manifest also in other magnetically uniaxial high-anisotropy ferromagnets.

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