Magnetic properties of single-crystal powders of $YFeO_3$

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A study has been made of the magnetic properties of single-crystal powders of yttrium orthoferrite, of dimensions from 0.25 to 1400 μ. From an analysis of the results of the measurements and also of results obtained earlier [1] it is deduced that over a broad range of dimensions, from the critical to the absolutely single domain, thermally demagnetized powders contain particles with a metastable domain structure (multidomain, and single-domain with nuclei of the opposite magnetic phase). The simultaneous presence of multidomain and single-domain particles leads to magnetization curves with sharply defined sections of easy and of difficult magnetization. With decrease of the powder size, the concentration of particles with a metastable structure decreases. In the finest powders there are particles that become remagnetized in a field of the order of the anisotropy field. This indicates the possibility of a realization of the absolutely single-domain structure in such particles. It is shown also that as a result of improvement of the crystal structure of the particles by etching and annealing, there occurs in the powders a decrease of the number of particles with a metastable domain structure; the displacement of domain boundaries in multidomain particles is facilitated, and the formation of remagnetization nuclei is impeded.

INTRODUCTION

In recent years much progress has been made in the study of domain structure in ferromagnets, and this has made possible the explanation of many of their magnetic properties. An exception is particles that possess a single-domain structure or nearly so; their magnetic properties have still been little studied. This results from the fact that in ordinary ferromagnets the dimension of a single-domain particle is very small, less than one micron. These difficulties can be overcome by investigation of the orthoferrites of rare-earth metals and yttrium, which have a small ferromagnetic moment ($I_S \sim 10$ G) and a quite high value of the magnetic-anisotropy constant ($K \sim 10^5$ erg/cm^3). Thanks to this combination of properties, the single-domain state occurs in comparatively coarse particles (hundreds of microns). On such particles of yttrium orthoferrite ($YFeO_3$) it has been possible to observe the domain structure visually[1] and to establish the important laws relating to the behavior and to the nature of the remagnetization nuclei[2].

It is obviously of interest to study the magnetic properties of powders composed of single-domain or nearly single-domain particles. Such a study has been made in the present paper of $YFeO_3$ powders composed of monocrystalline particles of various dimensions and consequently possessing various types of domain structure: from the absolutely single-domain (according to theoretical estimates) to the multidomain (according to visual observation of the domain structure).

SPECIMENS AND METHOD OF MEASUREMENT

Monocrystalline powders of various degrees of coarseness (see table) were obtained by mechanical grinding of the original coarse crystals, grown by the method of spontaneous crystallization. Separation of the powders according to coarseness was accomplished by means of sieves (powders 1–4) and by settling in a liquid (powders 5–8). The mean dimension of the particles in powders 5–8 was determined from volume-distribution curves of the particles. In all the powders, the particles had a nearly equiaxial shape. For preparation of the specimens, approximately 100-mg suspensions of the powder were taken. The powder was sealed with paraffin into aluminum cups. To produce magnetic texture, the specimens were heated until the paraffin melted and were then cooled in a constant magnetic field.

Measurements of the magnetization curves and hysteresis loops of isotropic and magnetically textured specimens were made by the ballistic method. The magnetic field was produced by a solenoid (to 1 kOe) and an electromagnet (to 35 kOe). To magnetize the specimens with a stronger magnetic field, apparatus for pulsed magnetic fields was used (to 140 kOe). Demagnetization of the specimens was accomplished by heating them to 400°C (the Curie point of $YFeO_3$ is $\Theta = 375$°C) and subsequently cooling them in a magnetic shield—thermal demagnetization.

Only powders 1–4 underwent etching and annealing. The etching was done in orthophosphoric acid at temperature 130°C, the annealing in air at temperatures 600–1200°C.

EXPERIMENTAL RESULTS

The important characteristics of the $YFeO_3$ powders are given in the table. The degree of texture λ was defined by the formula $\lambda = (\sigma^{\parallel}_{rm} - \sigma^{\perp}_{rm})/\sigma^{\parallel}_{rm}$, where $\sigma^{\parallel}_{rm}$ and $\sigma^{\perp}_{rm}$ are, respectively, the maximum specific remanent magnetizations of the specimen along and perpendicular to the texture axis. It is evident that with decrease of the particle dimensions the value of λ decreases, and in the finest powders 7 and 8 it is not possible to obtain magnetic texture. The magnetic susceptibilities $\chi^{\parallel}$, $\chi^{\perp}$, and χ^{x} were measured respectively

Some magnetic characteristics of powder specimens of yttrium orthoferrite

Powder number	Particle size, μ	Mean particle dimension, μ	Textured						Isotropic			
			λ	$\chi^{\parallel}\cdot 10^5$, G cm^3/g Oe	$\chi^{\perp}\cdot 10^5$, G cm^3/g Oe	$\sigma^{\parallel}_{rm}$, G cm^3/g	H_c, kOe	H_r, kOe	$\chi^{x}\cdot 10^5$, G cm^3/g Oe	σ^{x}_{rm}, G cm^3/g	H_c, kOe	H_r, kOe
1	1100–1600	1400	0.99	1.2	1.6	1.40	0.38	0.38	1.4	0.70	0.44	0.44
2	400–630	540	0.99	1.2	1.6	1.40	0.70	0.70	1.6	0.70	0.90	0.90
3	160–200	182	0.98	1.2	1.6	1.40	1.58	1.58	1.4	0.70	2.08	2.10
4	50–63	57	0.95	1.2	1.6	1.40	2.80	2.85	1.5	0.70	3.50	3.70
5	—	25	0.82	1.3	1.6	1.15	6.30	7.00	1.5	0.66	8.00	10.0
6	—	7	0.79	1.3	1.4	1.05	9.20	10.4	1.6	0.62	11.0	14.8
7	—	1	0.12	—	—	—	—	—	1.4	0.37	19.0	30.5
8	—	0.25	0.10	—	—	—	—	—	1.6	0.33	21.0	35.5

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along and perpendicular to the axis of magnetic texture of the textured specimens and on the isotropic specimens. These susceptibilities are due to reversible rotation of the magnetic moments of the Fe sublattices. Within the limits of experimental error, the susceptibilities are independent of the field, as is indicated by the linear form of the dependence $\sigma(H)$ in Fig. 1 (see also[3]). In agreement with the results of a study of the anisotropic properties of single crystals[4], it may be concluded that in powder specimens with $\lambda = 1$, $\chi^{\parallel}$ is determined entirely by the process of collapse of the magnetic moments of the sublattices. (This process has no effect on the hysteresis properties of single crystals when the field is oriented along the axis of easy magnetization. In $YFeO_3$, collapse of the sublattices should become complete in a field $\sim 6 \times 10^6$ Oe equal to the exchange-interaction field.) In the remaining cases, χ includes within it a susceptibility due to reversible rotation of the spontaneous moment σ_S.

From the table it is seen that for powders 1–4, in which $\lambda \approx 1$, $\sigma^{\parallel}_{rm} = 2\sigma^{x}_{rm}$, where σ^{x}_{rm} is the maximum remanent magnetization of an isotropic specimen. This equality indicates that in the state of remanent magnetization the powders consist of single-domain particles, and therefore we may take as the value of σ_S the value 1.4 G-cm^3/g. If we use the equality $2\sigma^{x}_{rm} = \sigma_S$ to determined σ_S in powders 5–8, for which $\lambda < 1$, we find that with decrease of the dimension of the powders the value of σ_S drops[1)].

The table shows also the values of the coercive force H_c and of the demagnetizing field H_r, after removal of which the specimens remain demagnetized. Figure 2 shows magnetization curves j(H) (circles) and remanent-magnetization curves $j_r(H_m)$ (points) (H_m is the amplitude of the previously applied magnetizing field), measured along the texture axis of specimens of powders 1–4, previously thermally demagnetized. The magnetization is given in relative units: $j = (\sigma - \chi H)/\sigma^{\parallel}_{rm}$, $j_r = \sigma_r/\sigma^{\parallel}_{rm}$, where σ_r is the specific remanent magnetization. It is evident that with decrease of the powder size, magnetization becomes more difficult. At the same time, beginning with powder 2 there appears on the curves a clear break, separating them into two sections: a section A of relatively easy magnetization, in the field range up to $H \sim 0.1$ kOe, and a section B of subsequent more difficult magnetization. With decrease of the powder size, the relative contribution of section A decreases, and correspondingly the contribution of section B to the $j(H)$ and $j_r(H_m)$ curves increases. Reversible processes are observed only within the limits of the sections A, since $j > j_r$ at given H_m. Application of a stronger field suppresses reversible processes ($j = j_r$).

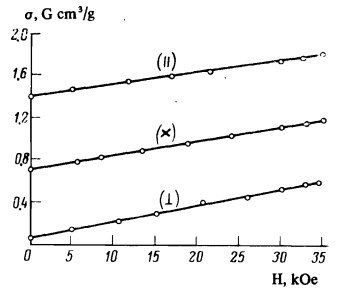

FIG. 1. Field dependence of specific magnetization of powder specimens 4: (||), along texture axis; (⊥), perpendicular to the texture axis; (X), isotropic specimen. The measurements were made in the direction of a previously applied field sufficient to saturate the specimens.

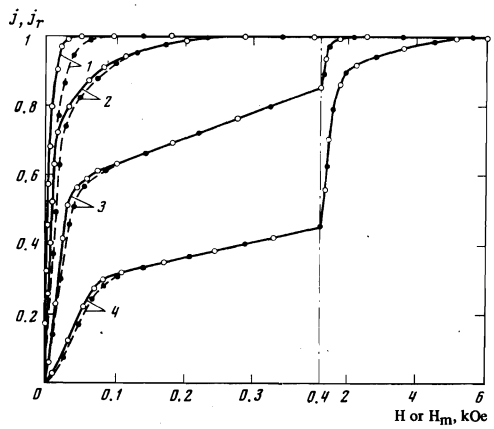

FIG. 2. Magnetization curves j(H) (○) and remanent-magnetization curves $j_r(H_m)$ (●) of textured specimens of powders 1–4. Here and below, the numbers on the curves correspond to the numbers of the powders in the table; j and j_r are in relative units; the vertical dot-dash line indicates a change of scale.

Figure 3 shows $j_r(H_m)$ curves for isotropic specimens of all the powders. For powders 1–4 the character of the curves is the same as in Fig. 2. The difference consists entirely in the fact that the magnetization of the isotropic specimens proceeds with more difficulty, and the transitions between sections A and B are spread out more. With decrease of the size, beginning with powder 5, section A practically disappears; magnetization of the powders becomes more and more difficult.

Curves $j_r(H_m)$ were also measured on isotropic specimens consisting of particles in a state of remanent magnetization. To prepare such specimens, the original specimens were first magnetized to saturation by a field, then heated until the paraffin melted, and the powder was carefully agitated. As a result, before application of a field the specimens possessed no resultant magnetic moment. Figure 4 shows $j_r(H_m)$ curves measured on specimens of powders 6–8 prepared by this method (crosses); here also, for comparison, are shown $j_r(H_m)$ curves measured on previously thermally demagnetized specimens (circles). It is seen that previous magnetization of the particles leads to an appreciable impeding of the magnetization of the specimens. This effect is relatively large in coarse powders and decreases with decrease of their size, so that for the finest powder 8 the $j_r(H_m)$ curves measured on specimens with different initial states of the particles coincide.

Figure 5 shows the demagnetizing branches $j(-H)$ of the limiting hysteresis loops (circles) and the corre-

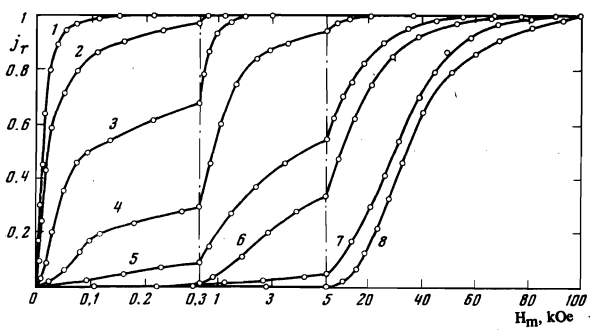

FIG. 3. Remanent-magnetization curves of isotropic specimens of powders 1–8. j_r is in relative units; the vertical dot-dash line indicates a change of scale.

sponding remanent-magnetization curves $j_d(-H_m)$ (points), measured on textured powder specimens 1–4 ($j_d = \sigma_d/\sigma^{\parallel}_{rm}$, σ_d is the remanent magnetization measured after removal of the field). It is seen that for each value of H_m, $j = j_d$; that is, the remagnetization of the specimens proceeds irreversibly. The $j_d(-H_m)$ curves for isotropic specimens are shown in Fig. 6. From a comparison with the preceding figure it is evident that remagnetization of the isotropic specimens is hindered to a greater degree. With decrease of the particle size, remagnetization of the specimens is greatly hindered. Measurements showed that in magnetization from the thermally demagnetized state, in relatively coarse powders, σ_{rm} is reached before the limiting H_c is reached; that is, for such powders a dependence of H_c on H_m is observed. With decrease of the powder size, this dependence gradually disappears.

The magnetic properties of the powders can be greatly changed by etching and annealing them. Thus Fig. 7 shows j(H) curves measured on isotropic specimens of powder 4 before and after 20 minutes of etching. (To judge from the change of mass of the powder, the particle dimension changed inappreciably as a result of etching: from 57 to 52 μ). In both cases the curves were measured after thermal demagnetization of the powder. It is seen that etching leads to a decrease of the relative contribution of section A to the j(H) curve; the magnetization process on this section is facilitated, whereas on section B, on the contrary, it is impeded. Figure 8 shows the effect of etching on the

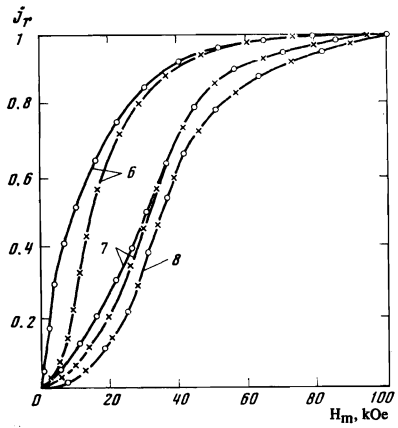

FIG. 4. Remanent-magnetization curves of isotropic specimens of powders 6–8, measured with initial thermally demagnetized (○) and remanently magnetized (X) states of the particles. j_r is in relative units.

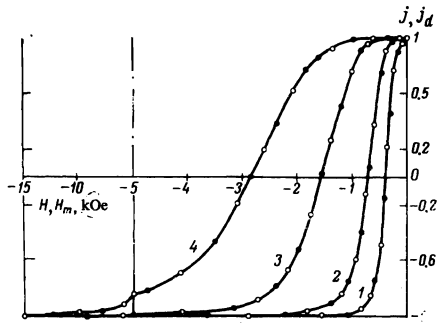

FIG. 5. Demagnetizing branches of limiting hysteresis loops j(−H) (○) and corresponding remanent-magnetization curves $j_d(-H_m)$ (●) of textured specimens of powders 1–4. j and j_d are in relative units; the vertical dot-dash line indicates a change of scale.

H_c of textured specimens of powders 1–4. The absolute increase of H_c is larger in the fine powders than in the coarse, and as a result the character of the $H_c(d)$ curves is practically unchanged after the etching.

Annealing of the powders has, on the whole, the same effect on their magnetic properties as does etching[2)].

DISCUSSION OF RESULTS

Before passing on to a discussion of the magnetic properties of powders, we shall present the principal results obtained in a study of the domain structure of individual monocrystalline $YFeO_3$ particles of dimension 30 to 800 μ [1]. The form of the domain structure after thermal demagnetization and its change with field were different for particles of different dimensions. After thermal demagnetization, coarse particles with $d > d_c \sim 300\ \mu$ (d_c is the critical dimension for the single-domain state) were always multidomain. Particles of dimension $d < d_c$ possessed a stable single-domain structure and also a metastable multidomain structure. With decrease of the particle dimension there was an increase of the probability of observing a single-domain structure in the particles.

On application of a field, magnetization of the particles with a multidomain structure proceeded by displacement of domain boundaries. Magnetization of the particles with a single-domain structure consisted in discontinuous remagnetization of them (we refer to particles whose σ_s direction was antiparallel to the orientation of the field). For some single-domain particles, the field for this jump was smaller than the jump field on the limiting hysteresis loop. This indicates the presence in the particles of metastable nuclei, which originated during the cooling from the Curie point.

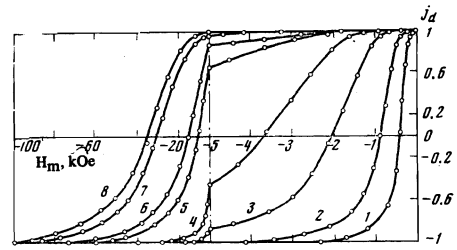

FIG. 6. Remanent-magnetization curves of isotropic specimens, corresponding to limiting hysteresis loops. j_d is in relative units; the vertical dot-dash line indicates a change of scale.

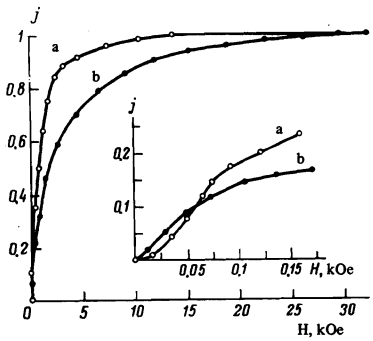

FIG. 7

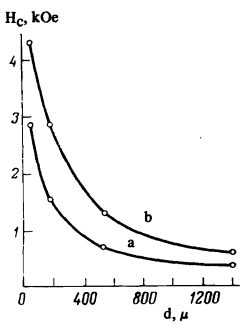

FIG. 8

FIG. 7. Magnetization curves j(H) of isotropic specimens of powder 4: a, before etching; b, after etching (j is in relative units).

FIG. 8. Dependence of coercive force of textured specimens on powder size: a, before etching; b, after etching.

After magnetization to saturation, all the particles possessed a single-domain structure. The remagnetization of the particles proceeded discontinuously. The field for the jumps was smaller than the anisotropy field $H_a = 2K/I_S$ (100 kOe for $YFeO_3$); this indicates the nucleation character of the remagnetization process of the particles.

Starting from what has been set forth about the peculiarities of the domain structure of nearly single-domain particles, we shall analyze the results obtained in the present paper on powder specimens of $YFeO_3$. After thermal demagnetization, powder 1, with particle dimension $d > d_c$, consists entirely of multidomain particles. In consequence of this, magnetization proceeds relatively easily (Fig. 2) by partially reversible displacement of boundaries ($j > j_r$). With increase of the field, the particles go over to the metastable single-domain state; this explains the quite rapid increase of j_r and the attainment of $j_r = 1$ (Figs. 2 and 3).

The presence of two sections on the $j(H)$ and $j_r(H_m)$ curves of powders 2—4, which have dimensions $d \lesssim d_c$, indicates that the original specimens contain a mixture of multidomain and single-domain particles. In sections A, magnetization occurs by displacement of boundaries in many-domain particles; while in sections B, it occurs by the appreciably more difficult irreversible ($j = j_r$) discontinuous remagnetization of single-domain particles (and specifically, of those particles whose σ_S directions are opposite to the direction of the field). The decrease of the relative contribution of sections A to the $j(H)$ and $j_r(H_m)$ curves indicates a decrease in the multidomain-particle content in the powders with decrease of their dimension.

The absence of sections of type A on the $j_r(H_m)$ curves of powders 5—8 (Fig. 3) shows that they consist entirely of single-domain particles, and consequently the form of the $j_r(H_m)$ curves is determined entirely by the difficulty of discontinuous remagnetization of the particles. In an overwhelming majority of the particles, this remagnetization has a nucleation character. Nuclei originate during the remagnetization process and also can exist in latent form. The possibility of the existence of such nuclei in thermally demagnetized particles is indicated by the noncoincidence of the $j_r(H_m)$ curves (Fig. 4) measured on specimens with different initial states of the particles. Obviously a preliminary magnetization of the particles leads to annihilation of nuclei, as a result of which subsequent magnetization of the specimens is impeded. The observed greater and greater coincidence of the $j_r(H_m)$ curves with decrease of the powder size indicates that after thermal demagnetization there is a decrease in the concentration of single-domain particles containing latent nuclei, culminating in a complete absence of such particles in powder 8.

According to theoretical ideas[6], in particles of dimension $d \leq d_0$, where d_0 is the dimesion for absolute single-domain character, the remagnetization occurs by uniform rotation of the magnetization, and the maximum jump field should be equal to H_a. For $YFeO_3$, the value of $d_0 \sim 1\ \mu$. Of the powders investigated, only powders 7 and 8 have dimension $d \sim d_0$; and only in these powders are there particles with jump field of order $H_a = 100$ kOe (Fig. 3). This allows us to suppose that the powders mentioned contain a certain number of particles with absolutely single-domain structure.

The results presented show that in all the powders, in the state of remanent magnetization the particles are single-domain. Their remagnetization along the limiting hysteresis loops (Figs. 5 and 6) occurs as a result of formation and subsequent discontinuous growth of nuclei of remagnetization. But in the case of powders 7 and 8, as was just indicated, remagnetization of a certain number of particles is possible by uniform rotation of the magnetization.

Defects of the crystalline lattice have a great effect on the magnetic properties of the particles, as is evidenced by the change of magnetic properties of the powders on etching and annealing. The effectiveness of etching shows that the defects are localized predominantly in a surface layer of the particles; this is natural when the method of obtaining them is by mechanical grinding. The influence of defects shows up, on the one hand, in the fact that in thermal demagnetization they promote the formation, in particles with $d < d_c$, of a metastable domain structure (multidomain, and single-domain with latent nuclei of the opposite phase); and on the other hand, the defects impede the displacement of domain boundaries and facilitate the process of formation of nuclei[2]. In fact, it is evident from Fig. 7 that after etching there was a decrease of the contribution of section A to the $j(H)$ curve: that is, there was a decrease of the concentration of particles with a metastable multidomain structure. At the same time, magnetization in this section, which proceeds by displacement of domain boundaries in the particles, was facilitated. The impeding of the magnetization process on section B was caused both by a decrease of the concentration of single-domain particles containing nuclei of the opposite phase, and by an impeding of the nucleation process in particles not containing such nuclei. The impeding of this process in consequence of improvement of the crystalline structure of the particles is attested by the increase of the H_c of the powders after etching (Fig. 8) and annealing.

It has been repeatedly emphasized above that with decrease of the powder size there is a pronounced change of the magnetic properties. It is possible to distinguish two causes responsible for this change: a) The nature of the defects in the particles changes (how, specifically, this expresses itself is at present difficult to answer). The reality of this cause is indicated by the effect of etching and annealing, which practically, without change of the dimension of the particles, lead to basically the same change of their magnetic properties as is observed with decrease of dimension. b) Even without change of the nature of the defects in the particles, changes of the magnetic properties were to be expected because of the fact that in the majority of the powders the dimension of the particles $d < d_c$. The existence in such particles of a metastable domain structure, as also the formation of remagnetization nuclei, is energetically the less advantageous, the smaller the dimension of the particle in comparison with d_c (or the closer it is to d_0). It is necessary to emphasize, however, that the dependence on size in this case can show up only in the presence of defects in the particles. If the particles were ideal, then the conditions for existence of metastable domain structures would not exist in them, and the remagnetization, independently of the dimension, would always occur at field H_a (since $K \gg I_S^2$).

[1)]Neither x-ray nor thermomagnetic analyses give sufficient grounds for asserting that any new phase occurs in fine powders. If we take into account that the value of σ_S in orthoferrites is sensitive to rhombic distortions of the lattice [5], we may suppose that the drop in σ_S in our case is due to a decrease of the noncollinearity of the magnetic moments of the sublattices in a region of defects that lead to the distortions mentioned.

[2)]After annealing at temperatures above 600°C, apparently in consequence of a partial loss of oxygen and transformation of some of the Fe^{3+} ions to Fe^{2+}, there was observed in the $YFeO_3$ powders the appearance of a new magnetic phase with $\sigma_S \sim 12$ G cm^3/g and Curie point ~200°C. The amount of the phase depended on the annealing temperature and on the powder size. After a short-duration etching of the powders, the phase disappeared. These facts indicate that the new phase appeared on the surface of the particles.

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