Model of interactions in nanometric particles of barium hexaferrite

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Abstract

Magnetic interactions in nanostructured Ba hexaferrite systems with partially coupled particles are studied. In this kind of systems, there are regions with lower effective magnetic anisotropy $K_{\text{eff}}$ where nucleation of magnetization reversal occurs. The Preisach distribution functions were measured for samples with different irreversible susceptibility behavior. Several peaks in the Preisach distributions were identified and were associated with different particle clusters. The coercive fields of these clusters were associated with $K_{\text{eff}}$.

A model was developed linking $K_{\text{eff}}$ with the exchange-coupled volume ($\beta$) between two neighboring particles and the number of particles in clusters.

The behavior that followed the best physical interpretation led to conclude that magnetization reversal starts in the exchange-coupled volume $\beta$ between two neighboring particles and then propagates to the rest of the particle.

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1. Introduction

The magnetic properties of granular or particulate systems, nanostructured single-phase or composite systems are strongly affected by interparticle interactions such as dipolar and exchange interactions that can assist changes in the magnetization state of the system.

Although the ideas behind exchange interactions are simple, most of the theoretical work done is based on micromagnetic modeling, particularly when the exchange-spring behavior is modeled in order to reveal the correlation between interactions and grain structure in composite magnets (see, for example, Refs. [1,2] and references therein).

Interphase dipolar interactions in hard–soft nanocomposite systems are observed to produce displacements of the hysteresis loop when the hard phase consists of randomly oriented nanoparticles embedded in a larger particle size soft
matrix [3]. This behavior was associated with stray fields in the soft phase around the hard phase [1,3]. These stray fields are strongly dependent on the geometry of the inhomogeneities. It was shown that inclusions with edges and corners produce larger demagnetizing fields than spherical inclusions [1].

Nanostructured single-phase or composite systems can be affected by exchange interactions between particles. Uncoupled particles in a single-phase hard magnetic material have high coercivity and a value of remanence $M_r$ that is half of saturation magnetization $M_S$; i.e.

$$M_r = \frac{1}{2} M_S.$$  

Hard–soft composites with uncoupled particles have $M_r = 0.5 M_S V_h$, where $V_h$ is the volume fraction of the hard magnetic phase. If the particles are strongly coupled, remanence is enhanced above the mentioned value, while high coercivity is preserved (see, for example, Refs. [4,5]).

From experience it is known that the coercive field $H_c$ of hard magnetic materials cannot be described by the nucleation field of single domain particles, given by Brown’s equation

$$H_c = 2 \frac{K_1}{M_S} - N_{\text{eff}} M_S,$$

where $K_1$ is the first anisotropy constant and $N_{\text{eff}}$ is the particle’s effective demagnetizing factor.

To explain this discrepancy, two models have been proposed (see, for example, Ref. [6]):

1. The nucleation model, where regions of reduced magnetocrystalline anisotropy constant are considered.
2. The global model [7], where pre-existing nuclei are considered and only a critical field is required to expand them.

The main difference between the nucleation model and the global model is that the former links the coercive field to the local changes in magnetocrystalline anisotropy while the later assumes a thermal activation mechanism for the expansion of nuclei of inverse magnetization.

The nucleation model predicts a modification to Brown’s equation known as the “modified Brown’s equation” asserting that the coercive field is given by [8]

$$H_c = 2 \frac{K_1}{M_S} x_\phi x_K x_{\text{ex}} - N_{\text{eff}} M_S,$$  

(1)

where $x_\phi$ takes care of the grains’ orientation distribution in the magnet (for a randomly oriented structure is equal to 0.5); the coefficient $x_K$ takes into account the reduction in anisotropy in the regions near internal surfaces, as grain boundaries and interphases. The third coefficient, $x_{\text{ex}}$, is used to describe the effect of exchange coupling between neighboring grains on the coercive field of the magnet. For alloys of Nd$_2$Fe$_{14}$B + Fe it is found that $x_{\text{ex}} \approx 0.3$ [9]; when the mean grain size of the hard phase varies between 25 and 40 nm $x_{\text{ex}} \approx 0.32–0.35$ and when the mean grain size goes up to 60 nm $x_{\text{ex}}$ reduces to 0.3 [5].

The effect of exchange interactions between coupled grains of hard magnetic materials can be visualized as a wall-like magnetic moment distribution in the volume next to the interface between grains. Those grains have a different easy axes orientation and when they are exchange coupled, the field needed to reverse the magnetization is drastically reduced [9]. Coercivity decreases as the exchange coupling increases.

Ignoring magnetostatic interactions, the general behavior of coercivity in nanostructured two-phase systems was analyzed using the concept of the exchange correlation length in both phases [11]. The effective anisotropy constant of the system, $K_{\text{eff}}$, depends on the number of particles that are in contact with each other, the crystal size $D$ and the characteristic length $l_K$—the anisotropy correlation length is the leading exchange length in hard magnetic materials [10]— defined as

$$l_K = \sqrt{\frac{A}{K_1}},$$

where $A$ is the exchange constant and $K_1$ is the first anisotropy constant.

Systems with completely coupled particles occur when $l_K > D$ and when the particles are uncoupled, it is $l_K \ll D$ and every particle magnetizes independently. An intermediate case occurs for values of $l_K$ of the order of $D/10$. In this case, the particles are partially coupled and there exists a superficial
layer around each particle (of thickness of the order of $l_K$) in which, as a consequence of the misalignment among the directions of the easy axis at both sides of the particle edge, the anisotropy diminishes [11,12]. As a result of this reduction in anisotropy, the regions contribute with lower nucleation fields for magnetization reversal.

As a general rule, coercivity has been used as a tool to estimate $K_{eff}$ in systems under study, not taking into account that the coercive field depends on the entire system. However, there exists a way to describe the magnetic behavior of a system of particles considering both the coercivity of each particle and the internal field acting on them. This can be accomplished by using the Preisach model [13,14] once the Preisach distribution function, $f(h_c, h_u)$, of coercive ($h_c$) and interaction ($h_u$) fields for the particles is known.

In a previous work by Bertorello et al. [15], the authors observe complex effects on the Preisach distribution function of samples of Ba hexaferrite with different degrees of sintering. They suggest that these effects are originated by the exchange interactions among particles with different number of neighbors.

In this work, our aim is to study magnetic interactions by systematically applying the previously obtained results [15]. The chosen system is Ba hexaferrite where the structure of nanoscale particles is in the range where the relation $l_k < D$ is valid. In these systems, partially coupled particles are present and nucleation of magnetization reversal occurs in regions with $K_{eff} < K_1$. By calculating Preisach distribution functions, we are able to identify the coercive fields of particle clusters and to link those coercive fields with $K_{eff}$ by proposing a model that can explain interactions between particles.

### 2. Description of the studied systems

Our interest is to study magnetic interactions in Ba hexaferrite nanoscale-particle systems in which different degrees of interaction are present. One way of producing such interactions is by allowing the sintering of particles. Different degrees of sintering give rise to a distribution of clusters with different number of particles that interact with each other. These clusters behave differently when a magnetic field is applied; in each sample there are clusters that act as having an effective anisotropy constant $K_{eff}$ which depends on the number of particles that are in contact amongst each other, the width of the coupled regions and the strength of the exchange intergranular coupling. In this work, different distributions of clusters are obtained by varying the sintering conditions.

We assume a continuous distribution of magnetization inversion fields due to a distribution of effective anisotropy constants. Thinking in terms of a Preisach model, those inversion fields can be identified with the coercive fields $h_c$ when the magnetostatic interactions $h_u$ are zero. Then, calculating the Preisach distribution $f(h_c, h_u)$ allows us to identify the distribution of magnetization inversion fields by means of $f(h_c, h_u = 0)$.

As usual, the Preisach model describes our system through a set of elementary non-symmetric square loops each one representing an elemental magnetic moment characterized by the coercive field $h_c$ and the interaction field $h_u$. The whole system is described by the Preisach distribution function $f(h_c, h_u)$ which tells us how many elementary loops have coercive fields between $h_c$ and $h_c + dh_c$ and interaction fields between $h_u$ and $h_u + dh_u$. The magnetization of the system under the effect of an applied field $H$ is then written as

$$M(t) = 2M_S \int_0^\infty d h_c \int_0^{b(h_c)} f(h_c, h_u) \, dh_u. \quad (2)$$

The boundary $b(h_c)$ is a staircase line [14] that divides the region where the elemental magnetic moments point to the same direction than $H$ (direction) from the region where they point to the opposite direction (−direction). This boundary is a function of time through the magnetic past history [13,14].

Calculating the Preisach distribution function is easier if we change variables from $h_c$, $h_u$ to $\alpha = (h_u + h_c)$, $\beta = (h_u - h_c)$. In terms of these new variables it is

$$f(\alpha, \beta) = -\frac{\partial^2 M(\alpha, \beta)}{\partial \alpha \partial \beta},$$
where \( M(x, \beta) \) is the magnetization of the sample at a point \((x, \beta)\) of a first-order reversal curve (FORC).

The Preisach distribution function will allow us to discuss about the nature of the interactions and the magnetization reversal process.

3. Experimental

The considered samples are the same as the ones used in the work mentioned in Ref. [15]. Sample M1 of nanostructured barium hexaferrite was obtained by milling the elemental oxides (\( \text{Fe}_2\text{O}_3 \) and \( \text{BaCO}_3 \)) in stoichiometric proportions in a planetary ball mill and performing a heat treatment at 1000°C in air for 1 h. This sample is composed of highly crystalline phase M and very small amounts of hematite, with a mean crystal size of 50 nm.

Other samples of Ba hexaferrite + hematite were obtained after milling \( \text{Fe}_2\text{O}_3 \) and \( \text{BaCO}_3 \) + 20 wt% Fe and then heating at 1000°C in air atmosphere. Sample MF1 was obtained by first heat-treating the loose powder for 1 h and then compacting it into platelets 1–2 mm thick. Sample MF8 was obtained by first compacting the as-milled powder and then heat treating it for 8 h. In the first case, only limited sintering occurred and only some agglomeration of particles was observed. In the second case, the sintering process produced a solid sample, with an apparent density of 3.46 g/cm³, approximately 66% of the full density. X-ray diffraction performed on these samples showed that both of them consist of Ba hexaferrite and hematite, with mean crystal sizes of 50 (MF1) and 60 nm (MF8), values well below the monodomain particle size for Ba hexaferrite [18].

4. Results and comments

X-ray diffraction shows that all samples contain highly crystalline Ba hexaferrite and hematite approximately in proportion 95–5% in sample M1 and 80–20% in samples MF1 and MF8. As mentioned before, the mean crystal size as measured by line broadening applying the Scherrer formula gives 50 nm for M1 and MF1 and 60 nm for MF8. Remanent magnetization gives \( M_r/M_S = 0.55 \) in all cases. As the particles are randomly oriented that ratio should be 0.5. The modest 10% remanence enhancement is produced by a partial exchange coupling between Ba hexaferrite crystals. The exchange coupling occurs in the regions adjacent to the contact surface in between the crystals.

Figs. 1–3 show the Preisach distribution functions obtained for the three studied samples.

In order to check the validity of these Preisach distributions, we compared the measured values of the irreversible susceptibility \( \chi_{\text{irr}} \) with the calculated \( \chi_{\text{irr}}^{\text{i-calc}} \) using:

\[
\chi_{\text{irr}}^{\text{i-calc}} = \chi_{\text{tot}}^{\text{i}} - \chi_{\text{rev}}^{\text{i}}
\]

\[
\chi_{\text{irr}} = \frac{\partial M}{\partial H} - \chi_{\text{rev}} = 2 M_S \int_{0}^{\infty} f(h_c, h_c - H_i) \, dh_c - \chi_{\text{rev}}^{\text{i-calc}},
\]

where superscript \( i \) indicates derivatives with respect to the internal field \( H_i \), calculated by taking into account the demagnetizing field. The reversible susceptibility \( \chi_{\text{rev}} \) was determined by calculating the slope of a small loop performed at different fixed fields, after saturating the sample. A good agreement between \( \chi_{\text{irr}}^{\text{i}} \) and \( \chi_{\text{irr}}^{\text{i-calc}} \) is obtained, indicating that the Preisach distributions found to describe the three systems correctly.

As shown in Fig. 1, M1 has a Gaussian-shaped distribution function, with a maximum centered in \( h_c = 4100 \) Oe and standard deviation \( \sigma_c = 1000 \) Oe on the variable \( h_c \) and \( \sigma_u = 200 \) Oe on the variable \( h_u \). The peak value is very close to the field for which the irreversible susceptibility on this sample has a maximum. This continuous Gaussian-like distribution of \( h_c \) could be attributed to the fact that this sample is composed of phase M with only 5% hematite and the partial sintering has produced a continuous distribution of the effective anisotropy \( K_{\text{eff}} \).

The Preisach distributions obtained for MF1 and MF8 (Figs. 2 and 3, respectively) are more complex than the usual Preisach distributions reported in the literature for systems composed.

\(^{1}\)The measurement of a FORC starts by saturating positively the sample, then ramping down the applied field up to a value \( H = z \) and then recording the values \( M(x, \beta) \) when the field is increased up to a value \( H = \beta = -z \). For more details the reader may consult Ref. [13–17].
of a single magnetic phase. The one corresponding to sample MF1 has a narrow and high peak at 5300 Oe, a number of overlapping small peaks down to 2500 Oe and a distinct and low-intensity peak at 2000 Oe. Sample MF8 has a Preisach distribution with a succession of almost equally spaced distinct peaks of roughly the same intensity centered at different \( h_c \) from 4200 to 1500 Oe. The interaction field in both samples is low, with standard deviation not exceeding 200 Oe while the observed peaks have standard deviation in \( h_c \) not greater than 250 Oe.

The observed multiple peaks suggest us that they represent different groups of particle clusters that invert their magnetization at the fields \( h_c \) of the maxima. The sintering process has produced a distribution of cluster sizes, as sintering occurs among different number of particles. The origin of this kind of distributions lies in the fact that both MF1 and MF8 are composed not only of Ba hexaferrite but also of 20% hematite. This phase surrounds conglomerates of phase M with different number of particles preventing them from welding with each other during the sintering process. Also the pores in the samples play a role in the formation of the conglomerates. In MF1 there are more pores because this sample was prepared by first heat treating the powder and then compacting it. More conglomerates with few particles are expected in this case. This fact is reflected in the Preisach distribution of this sample because, as it can be seen in Fig. 2, the highest maximum is attained at high fields. On the other hand, MF8 was first compacted and then sintered, so in this case there was a smaller proportion of pores and a wider distribution of conglomerates that underwent the sintering without losing certain “individuality”. It is highly probable that each conglomerate will have a well-defined \( h_c \) value, the larger the number of particles per conglomerate the lower the corresponding \( h_c \).
5. Proposed interaction model and discussion

As mentioned before, the Preisach distributions obtained for samples MF1 and MF8 suggest that there is a distribution of clusters with different number of particles that invert their magnetization at different coercive fields, each type of cluster producing a peak in the Preisach distribution. Then, each peak corresponds to the $K_{\text{eff}}$ value associated with each type of cluster and is due to the existence of regions with lower coercivity produced by exchange coupling. The underlying idea is that the more neighbors are in contact with a certain particle, the more regions with a weakened anisotropy constant—and thus lower inversion field—will be. Therefore, a particle that is exchange-coupled with only one neighbor has a higher inversion field $h_c$ than a particle with two exchange-coupled neighbors, this one has a higher $h_c$ than one with three, and so on.

We identify the coercive field $H_{\text{c exp}}^c$ of each type of cluster with the maxima $h_c$ of every peak that appears in the Preisach distribution. Then, if the coercivity is defined by the effective anisotropy constant, from Eq. (1) we have:

$$K_{\text{eff}} = K_1 \chi_\phi \chi_K \chi_\text{ex} = \frac{M_S}{2} (H_{\text{c exp}}^c + N_{\text{eff}} M_S),$$

where $N_{\text{eff}} = \frac{3}{20} \ln(D/l_w)$ [10], being $D$ the mean particle size and $l_w$ the domain wall thickness. As the samples fabrication process does not favor any particular orientation we are dealing with randomly oriented structures, so it is $\chi_\phi = \frac{1}{2}$. This is valid not only for the sample as a whole but also for the particles that invert their magnetization at fields between $H_c$ and $H_c + dH_c$ because their number is of the order of $10^{14}$ or higher.

We assign the observed peaks in the Preisach distribution of MF1 and MF8 (see Figs. 2 and 3) to particles that interact with up to $n = 11$ neighboring particles. In the case of sample MF1, the
Preisach distribution (Fig. 2) shows a very high peak for a high value of $H_{\text{exp}}^c$ and considerable lower peaks for smaller fields. It seems reasonable that sample MF1 is formed by a great majority of clusters of few particles (one or two) because they did not have the chance to “stick to” as many particles as in MF8. The strongest peak in MF1 is observed at a value of $H_{\text{exp}}^c$ that corresponds to particles to which we assign no interacting neighbors because $K_{\text{eff}} \approx K_1/2$.

In Fig. 4, $K_{\text{eff}}$ given by Eq. (3) is plotted as a function of the assigned number of exchange coupled neighbors, $n$, that stick to a given particle. The data for both samples give a common linear dependence and this suggests that the exchange-coupled volume per particle is constant.

Let $\beta n$ be the volume fraction of the superficial layer of depth of the order of $l_K$ that has less anisotropy with respect to the total volume of the particle. The effective anisotropy constant inside the particle, $K_{\text{in}}$, and in the superficial layer affected by exchange coupling, $K_{\text{ex}}$, are given by

$$K_{\text{in}} = K_1 \beta_K \varkappa_{\phi} \quad (\text{as } \varkappa_{\text{ex}} = 1 \text{ inside the particle, in the uncoupled volume})$$

$$K_{\text{ex}} = K_1 \beta_K \varkappa_{\phi} \varkappa_{\text{ex}}.$$
Then, we may write \( K_{\text{eff}} \) as a weighted mean between coupled and uncoupled regions,\(^2\) as

\[
K_{\text{eff}}(n) = K_{\text{in}}(1 - \beta n) + K_{\text{ex}} \beta n \quad (6)
\]

or else

\[
K_{\text{eff}}(n) = K_{\text{in}} + \beta (K_{\text{ex}} - K_{\text{in}}) n. \quad (7)
\]

From this expression it is clear the linear relationship between \( K_{\text{eff}} \) and \( n \), in which \( K_{\text{in}} \) is the \( y \)-intercept and \( \beta (K_{\text{ex}} - K_{\text{in}}) \) is the slope. From the \( y \)-intercept of the line in Fig. 4 it results:

\[
K_{\text{in}} = 15.5 \times 10^6 \text{ G Oe}.
\]

Note that this result gives \( K_{\text{in}} \approx K_1/2 \) and \( z_K \approx 1 \) in the uncoupled volume (the region inside the particle).

The determination of \( K_{\text{ex}} \) requires an estimation of \( \beta \). For spherical particles, the volume affected by exchange coupling is a spherical casque of width \( 2.5 l_K \), where \( l_K = 4.9 \text{ nm} \) \([14]\). This casque’s width is considered as \( 2.5 l_K \) because it is in this width that lies all the energy stored in a domain wall \([14]\).

The ratio of the volume affected by exchange coupling to the particle volume is 0.87. If we consider a maximum of 11 neighboring particles, we can say that \( \beta \) is \( 11/1 \) of the volume of the spherical casque affected by exchange coupling. This reasoning gives an estimate of \( \beta = 0.08 \).

Now it is possible to evaluate \( K_{\text{ex}} \) from the second term of Eq. (6), giving

\[
K_{\text{ex}} = 5 \times 10^6 \text{ G Oe}.
\]

From the slope of the line given by Eq. (6) and the calculated values of \( K_{\text{in}} \) and \( K_{\text{ex}} \) we deduce:

\[
z_K \approx 1.
\]

The coefficient which accounts for exchange coupling, \( z_{\text{ex}} \), can be evaluated from the definition of \( K_{\text{ex}} \) given in expression (5), obtaining

\[
z_{\text{ex}} \approx 0.32.
\]

The results obtained for the parameters \( z_K \) and \( z_{\text{ex}} \) using the model proposed in this paper are based on evidence of clustering of particles obtained from the Preisach distributions. These results are somehow different to other authors’ who used only coercivity values for the whole sample in systems of particles in which exchange coupling occurs. In particular, \( z_K \) is usually found between 0.6 and 0.8, revealing the existence of zones of reduced anisotropy not linked to exchange coupling. In our case \( z_K \approx 1 \) means a high degree of crystallinity and low enough stray fields and/or surface defects as they are not capable of inducing noticeable changes in the anisotropy. This fact is especially true for the inner part of the particles where \( K_{\text{in}} \) is exactly \( K_1/2 \) due to the randomness of the structure. The outer shell may have some reduced anisotropy due to stray fields and surface defects but this effect is superimposed to the reduction in anisotropy due to exchange coupling, resulting in a value for \( z_{\text{ex}} \) that is of the same order than the one found for other hard magnets \([5,9]\). When the whole particle is exchange-coupled to its neighbors such detailed description cannot be made, then \( z_K \) is assigned to the whole particle and the final result is that the product \( z_K z_{\text{ex}} \) is in the range 0.18 – 0.25 \([5,6,20]\).

In the literature, \( z_{\text{ex}} \) is an empirical parameter that reflects the magnitude of the exchange interactions. The model presented here allows to relate this parameter with the interaction volume per particle and the number of neighbors each particle has. Accordingly, a given particle interacts with \( n \) neighbors, in an average volume \( \beta V \) with each of them (\( V \) is the particle volume). Magnetization reversal will start in the most favorably oriented volume \( \beta V \) with respect to the magnetic field.

Because of the exchange interaction of a given particle with \( n \) neighbors the spin distribution inside it is no longer uniform, so that the mechanism for magnetization reversal cannot be coherent rotation–except in an isolated particle.

We suggest that magnetization reversal is a process that starts in one of the exchange volumes \( \beta V \), the one with the most favorable orientation to invert its magnetization.

6. Conclusions

In this work, it is demonstrated the usefulness of the Preisach distribution to gain insight into the

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\(^2\)This kind of description has been previously used by Arcas et al. \([11]\) for two-phase materials and by Billoni et al. \([19]\) to study crystalline anisotropy in Nd\(_2\)Fe\(_{14}\)B + Fe compounds.
The demagnetizing process. The Preisach distribution function gives us direct information about the exchange interactions that occur in clusters of particles with different number of neighbors. In the studied system, Ba hexaferrite with particle volume of \(65 \times 10^{-18} \, \text{cm}^3\), the exchange interaction occurs in the volume of a superficial shell of width \(2.5 l_K\) and the interaction volume per particle is of the order of 0.08 of the particle volume.

Assuming an effective anisotropy constant \(K_{\text{eff}}\) as the weighted mean between coupled and uncoupled regions we are able to calculate the empirical factors that appear in the modified Brown’s equation.

It is worth mentioning that it was possible to ascertain interaction effects between neighboring particles that form clusters. This fact shows the usefulness of the Preisach distribution for studying interaction effects in magnetic particulate systems. The calculation of \(\alpha_{\text{ex}}\) and \(\alpha_K\) usually involves temperature-dependent coercivity measurements, but in this work we were able to obtain these coefficients from room-temperature measurements only.

Further improvements of the model presented here are based on how \(\beta\) and \(K_{\text{ex}}\) are related to the particular spin orientation distribution across grain boundaries and are currently being developed. That information will provide a relationship between the empirical factor \(\alpha_{\text{ex}}\) and the strength of the exchange-coupling mechanism.

References


