Magnetic study of $M$-type doped barium ferrite nanocrystalline powders

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We have studied the static magnetic properties of three different $M$-type doped barium ferrite compounds prepared by the glass crystallization method. The zero-field-cooled (ZFC) and field-cooled (FC) processes have been recorded at low field and they all show the typical features of a small particle system. The ZFC curves display a broad peak at a temperature $T_M$, which depends on the distribution of particle volumes in the sample. Isothermal magnetization curves $M(H)$ at several temperatures and saturation magnetization $M_s$ as a function of temperature have been measured for the Co-Ti sample (BaFe$_{10.4}$Co$_{0.8}$Ti$_{0.8}$O$_{19}$). The dependence on temperature of the macroscopic magnetic parameters has been analyzed. The distribution of blocking temperatures is studied from the derivative of the remanent-to-saturation magnetization ratio with respect to temperature and it is fitted to a lognormal distribution, leading to a mean blocking temperature ($T_B$) = (81 ± 40) K. The distribution of volumes of the magnetic unit is also obtained from this fitting. The dependence on temperature of the coercive field follows a $T^{-k}$-law below 35 K. The value of the $k$ exponent is discussed within the scope of two models: (i) the aligned case ($k$=0.5) and (ii) the random case ($k$=0.77).

I. INTRODUCTION

$M$-type barium ferrite BaFe$_{12}$O$_{19}$ has been widely studied because of its applicability in various technological fields, such as microwave devices, permanent magnets, and high-density magnetic and magneto-optic recording media. Many efforts have been devoted to the development of a synthesis procedure that leads to a better control of both particle size and morphology, since the conventional ceramic method does not fulfill these aims. Among them (see, for example, Refs. 4–6), the glass crystallization method (GCM) appears to be particularly successful in controlling the particle size, from the nanocrystalline regime (mean particle diameter of some tens of angstrom) to the microscopic region (some microns).

As regard to technological applications, BaFe$_{12}$O$_{19}$ powders consisting of an assembly of plateletlike single crystalline particles of about 1 µm are suitable materials for permanent magnets. Concerning magnetic recording, the ideal mean particle size is about 0.1 µm. Since the pure compound displays too high a coercive field $H_c$ which precludes its technological applications, BaFe$_{12}$O$_{19}$ is usually doped with Co$^{2+}$ cations, which sharply reduce its magnetic anisotropy. In this framework, the Co$^{2+}$-Ti$^{4+}$ doping scheme (leading to BaFe$_{12-x}$Co$_x$Ti$_x$O$_{19}$ samples, 0.1 $<$ x $<$ 1.0), is the most commonly used, although other schemes have also been tested, such as the Co-Sn $^{10,11}$ Co-Ti-Sn $^{14}$ and the Co-Ti-Sn-Ge $^{14}$ doping schemes. The first was designed in order to reduce the coercive field faster than the Co-Ti substitution, while the other two were studied so as to control the temperature coefficient $dH_c/dT$. As for the Co-Ti doping, the x=0.8 compound seems to be the best one for magnetic recording applications, since the magnetic structure is still ferrimagnetic, the Curie temperature is well above room temperature and the coercive field is sharply reduced to technologically achievable values. We note that Toshiba has announced the production of a 3.5-in barium ferrite floppy disk with 40 Mb of memory by the spring of 1993 (Ref. 15), which will increase the current memory capacity by about one order of magnitude.

In this paper, we study a particle size region that may lead us to further technological applications, as well as to new fundamental properties: the nanocrystalline region. GCM is proving to be an excellent method to obtain $M$-type doped barium ferrite powders with mean particle size ranging from about 80 to 300 Å (depending on both the thermal treatment and the doping cations), having a plateletlike shape and a narrow size distribution. We present the magnetic properties of three different compounds: (i) BaFe$_{10.4}$Co$_{0.8}$Ti$_{0.8}$O$_{19}$ (Co-Ti sample), (ii) BaFe$_{10.x}$Co$_{0.85}$Ti$_{0.45}$Sn$_{0.45}$O$_{19}$ (Co-Ti-Sn sample), and (iii) BaFe$_{10.4}$Co$_{0.8}$Ti$_{0.45}$Sn$_{0.25}$Ge$_{0.10}$O$_{19}$ (Co-Ti-Sn-Ge sample).

II. EXPERIMENT

All samples were prepared by the glass crystallization method. The GCM is characterized by homogenized melt fluxes of Fe$_2$O$_3$, BaO, B$_2$O$_3$ and of the corresponding oxides of the doping cations (for example, Ti$_2$O and CoO for the Co-Ti sample) at about 1300 °C, which were amorphized by rapid quenching in a two-roller equipment. Annealing the glass flakes above 550 °C led to the nucleation and growth of the borate and the hexaferrite phases. Barium ferrite particles crystallized to suitable sizes during this treatment and they were isolated by dissolving the

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matrix in dilute acetic acid in an ultrasonic field. After centrifugation, washing and drying, a fine powder of $M$-type doped barium ferrite particles with the required stoichiometry was obtained. A more detailed explanation on this procedure is given in Refs. 8 and 14, and references therein.

Magnetization measurements were carried out with an SHI S.Q.U.I.D magnetometer in the temperature range 4.2–300 K and in magnetic fields up to 50 kOe. The zero-field-cooled (ZFC) and field-cooled (FC) processes were recorded at low field (at about 35 Oe) in the same temperature range for the Co-Ti, Co-Ti-Sn, and Co-Ti-Sn-Ge samples, while the isothermal magnetization curves $M(H)$ at some given temperatures and the dependence on temperature of the saturation magnetization were recorded for the Co-Ti compound, in order to compare the experimental results to those reported in the literature concerning bulk powders.

**III. RESULTS AND DISCUSSION**

We display in Figs. 1(a)–1(c) the ZFC and FC magnetization data for all three compounds studied.

The ZFC curves show a wide maximum at $T_M$, thus indicating that the magnetic moment of each particle is blocked along its easy magnetization direction at a temperature $T_B$, which depends on particle volume, anisotropy, and orientation. As the samples are constituted of an assembly of crystallites that present a certain distribution of volumes $f(V)$, each crystallite is blocked at a different temperature $T_B$, which is not influenced by the easy magnetization direction in absence or in very low magnetic field. Then, we observe experimentally a distribution of blocking temperatures $F(T_B)$ providing a broad peak in the ZFC curve. The maximum of the curves is reached at $T_M \approx 195, 175, \text{and } 245 \text{ K for the Co-Ti, Co-Ti-Sn-Ge, and Co-Ti-Sn samples, respectively.}$ $T_M$ is related to the mean blocking temperature $\langle T_B \rangle$ through the distribution of particle volumes (see below). Transmission electron microscopy (TEM) shows that $T_M$ increases with mean particle volume $\langle V \rangle$ ($\langle V \rangle$ is about $1.1 \times 10^5, 0.88 \times 10^5, \text{and } 17.5 \times 10^5 \text{ A}^3$ for the Co-Ti, Co-Ti-Sn-Ge, and Co-Ti-Sn samples, respectively). Besides, the ZFC magnetization ($M_{ZFC}$) strongly decreases below the peak, since the superparamagnetic-ferromagnetic passage activate the anisotropy which force particle magnetization along the easy axes, which are randomly oriented. The relative decrease of $M_{ZFC}$ is also observed above $T_M$, as we approach the superparamagnetic region.

There also appears a clear irreversibility between the ZFC and FC measurements. The FC magnetization achieves a nearly constant value below a given temperature $T^* \text{ (which is always below } T_M \text{) and this value is much higher than the ZFC values.}$ The FC magnetization state is nearly an equilibrium state in which below $T^*$ almost all particles have only a positive projection of the magnetization along the magnetic field direction, while the ZFC magnetization state is not a true equilibrium state. If we record the evolution of $M_{ZFC}$ at a given temperature below $T_M$ as a function of time, this value will tend asymptotically to the corresponding FC magnetization value ($M_{FC}$). The magnetic irreversibility [Fig. 2(a)] is very small for the Co-Ti and Co-Ti-Sn-Ge samples at about room temperature, while it is still high for the Co-Ti-Sn compound, thus indicating that either some degree of magnetic correlation

![FIG. 1. Zero-field-cooled and field-cooled magnetizations as a function of temperature measured at 35 Oe for (a) the Co-Ti compound, (b) the Co-Ti-Sn-Ge compound and (c) the Co-Ti-Sn compound.](image-url)
is maintained or there are still a non-negligible amount of blocked particles. In fact, the temperature of the maximum of the ZFC ($T_M \approx 245$ K) is the largest of the three compounds studied.

Therefore, we may obtain a rough estimation of the extrapolated Curie–Weiss temperature $\theta$ only for the Co-Ti and Co-Ti-Sn-Ge compounds. Although at room temperature most of the particles are already superparamagnetic (see Figs. 1–2 and 6–8), we have to go to higher temperatures in order to accomplish a well-defined linear law $M_{FC}$ vs $T$ and a full superparamagnetic regime. We observe in Fig. 2(b) that the linear law is only accomplished between 275 and 300 K, and we find that the extrapolated ordering temperatures $\theta$ are about 174 and 179 K for the Co-Ti and Co-Ti-Sn-Ge samples, respectively. The positive sign indicates that magnetic interactions among particles are ferromagnetic, and the fitted $\theta$ values are high. The superparamagnetic regime will extend up to the Curie temperature $T_c$ ($T_c \approx 633$, 621, and 615 K for the Co-Ti, Co-Ti-Sn, and Co-Ti-Sn-Ge samples, respectively).\(^{16}\)

The dependence on temperature of the saturation magnetization $M_s$ for the Co-Ti sample, measured at 50 kOe, is displayed in Fig. 3. We assume that the decrease of $M_s$ below $T \approx 35$ K is due to the fact that we cannot saturate the sample, since we cannot rotate the magnetic moments of all blocked particles along the magnetic field direction, even at 50 kOe. In the inset of Fig. 3, $M_s$ is shown as a function of $T^{3/2}$, suggesting that the $T^{3/2}$-law\(^{17}\) does not account for the evolution of $M_s$. However, the linearity of $\log_{10} [M_s(35 \text{ K}) - M_s]$ vs $\log_{10} T$ above 120 K (Fig. 4) with a slope $\alpha \approx 2.7$ [where $M_s(35 \text{ K})$ is the saturation magnetization measured at $T = 35$ K and $H = 50$ kOe], might indicate that the observation of the $T^{3/2}$ term is precluded at low temperature due to relaxation effects.

![FIG. 2](image1)

![FIG. 3](image2)

![FIG. 4](image3)
while above ~120 K we observe the $T^{5/2}$ term. It should be noted that recent calculations,\textsuperscript{18} as well as recent experimental results,\textsuperscript{19} for ultrafine particles and clusters (some tens of angstrom) having fcc and bcc structures have shown that the spin wave picture may also be applied, with an $\alpha$ exponent in the demagnetizing law $T^\alpha$ which ranges from 3.0 for the smallest clusters (decreasing almost linearly with the inverse of the cluster diameter) towards the bulk value 1.5.

The isothermal magnetization curves $M(H)$ of the Co-Ti sample have been recorded at several temperatures below the maximum of the ZFC curve $T_M$. Virgin curves are shown in Fig. 5 and the coercive fields obtained from the hysteresis cycles are displayed in Fig. 6 (a). The dependence on temperature of the initial susceptibility $\chi_{in}$ (slope of the linear regime $M$ vs $H$ at low fields) is represented in Fig. 7. Figures 5 and 7 clearly indicate that $\chi_{in}$ rapidly increases with temperature, in such a way that, as the zero-field saturation magnetization (the value of the magnetization at zero-field extrapolated from the saturated regime) decreases with temperature, the $M(H)$ curve at a given temperature crosses all $M(H)$ curves corresponding to lower temperatures. This is experimentally observed when $T > 35$ K (Fig. 5), as expected from Fig. 3 ($M_s$ vs $T$).

The dependence on temperature of the coercive field $H_c$ is shown in Fig. 6(a). For monodisperse, noninteracting, ferro/ferrimagnetically ordered particles, coercivity is expected to depend on temperature as

$$H_c = H_c(0)(1 - AT^\alpha),$$

where $H_c(0)$ is the coercive field at $T = 0$, and $A$ is written as

$$A = [\beta k_B/(K_{eff} V)]^\alpha,$$

where $V$ is the particle volume and $\beta$ is a coefficient that depends both on the measuring time of the experiment $\tau_m$ and on the prefactor $\tau_0$ that governs the superparamagnetic relaxation through the relaxation time $\tau$ of the Arrhenius law:

$$\tau = \tau_0 \exp(K_{eff} V/k_B T).$$

The $k$ exponent in Eqs. (1) and (2) is 1/2 for an assembly of aligned particles\textsuperscript{20} and the coercive field follows the characteristic $T^{1/2}$-law. Pfeiffer has developed the case of an assembly of randomly oriented particles, obtaining that the coercive field also follows a $T^{k}$-law, with $k = 0.77$ (See Ref. 33). $H_c$ is plotted against $T^{1/2}$ and $T^{0.77}$ in the inset of Fig. 6(a) and in Fig. 6(b), respectively. Both approaches lead us to similar agreements with experimental results and they are followed only at the four lowest temperatures ($T < 35$ K), since Eq. (1) is correct when most of the particles are blocked. The ZFC curve [Fig. 1(a)], the initial susceptibility $\chi_{in}$ (Fig. 7) and the ratio $M_r/M_s$ [Fig. 8(a)] all suggest that this is accomplished at
low temperatures, far enough from the maximum of the ZFC curve ($T_M \approx 195$ K). The fitting of the experimental $H_c$ values with Eq. (1) leads to $H_c(0) = 5570$ Oe and $A = 0.119$ K$^{-1/2}$ for the $T^{1/2}$-law, and to $H_c(0) = 4690$ Oe and $A = 0.043$ K$^{-0.77}$ for the $T^{0.77}$-law.

Assuming the characteristic values of $\tau_0$ ($\tau_m \approx 10^{-9} - 10^{-13}$ s) and of the measuring time of the experiment ($\tau_m \approx 50-100$ s for S.Q.U.I.D magnetometry) $\beta$ may be estimated from $\beta = \ln(\tau_m/\tau_0)$ leading to $\beta = 25-34$. $\beta$ represents the ratio between the anisotropy energy and the thermal energy at which the relaxation time of a given particle is of the order of the measuring time of the experiment. This implies that, being the relationship between the two energies:

$$K_{eff}V = \beta k_BT,$$  

the particles with volume $V$ and anisotropy per unit volume $K_{eff}$ are blocked at a temperature $T$. Taking the usual value $\beta = 25$ (Ref. 20), although recent experiments show that $\beta$ may be larger, $19$ Eq. (2) and the experimental $A$ values give an average energy $\langle K_{eff}V \rangle$ of about $2.4 \times 10^{-13}$ erg (0.15 eV) and $2.1 \times 10^{-13}$ erg (0.13 eV) for the $T^{1/2}$-law and $T^{0.77}$-law, respectively. $\langle K_{eff}V \rangle$ represents the mean height of the energy barrier distribution.

Concerning the isothermal magnetization curves, $M$ may be written at low fields (below about 1000 Oe) as

$$M = \chi_{in}H,$$  

where $\chi_{in}$ is the initial susceptibility, which is shown, as a function of temperature, in Fig. 7. The initial susceptibility increases more than one order of magnitude between 6 and 210 K and follows the ZFC magnetization perfectly [see Fig. 1(a)]. We should remark that the isothermal magnetization curves have always been recorded in the same way: we cool the sample up to room temperature and, then, we cool it in zero field down to the measuring temperature. We assume that both $\chi_{in}$ and $M_{ZFC}$ variations come from the contribution of the superparamagnetic particles and this contribution increases with temperature up to $T_M$.

Above about 2000 Oe, the $M(H)$ curves were fitted to the law of approach saturation (LAS) for ferromagnetic and ferrimagnetic powders$^{21}$

$$M = M_0(1-A/H-B/H^2) + \chi_dH,$$  

where $M_0$ is the zero-field saturation magnetization and $\chi_d$ is the high-field differential susceptibility. $\chi_d$ is due to the contribution of noncollinear spins in the magnetic structure and it appears frequently in $M$-type doped ferrites as a consequence of the disruption of the collinear uniaxial magnetic structure when doping with diamagnetic cations. These cations induce the suppression of some superexchange paths that facilitate the magnetic equilibrium, leading to new noncollinear magnetic structures.$^{22}$ Apart from this contribution, surface effects arising from noncollinear surface spins are also important in small particles. The $A/H$ term is related to the existence of inhomogeneities in the microcrystals which reduce the mobility of the magnetization$^{23}$ and theoretically should vanish at high enough magnetic fields,$^{24}$ otherwise the magnetic energy necessary to saturate the sample would be infinite. This result has indeed been confirmed experimentally.$^{25}$ The $B/H^2$ term is related to the magnetic anisotropy and it may be written for a uniaxial hexagonal compound with $K_2 \ll K_1$:

$$B/H^2 = 1/15(H_c/H)^2C_B,$$  

where $H_c$ is the magnetocrystalline anisotropy field of a uniaxial system, with $H_c = 2K_1/M_0^{max}$, and $K_1$ is the first anisotropy constant. $H_{sh}$ represents the shape anisotropy field,$^{3}$ expressed as $H_{sh} = \Delta N M_0^{max}$, $\Delta N$ being the difference between the demagnetizing factors along the easy and hard directions of a particle. As a first approximation, we will take $\Delta N = 4\pi 0.54$ for the powder sample, corresponding to an aspect ratio (diameter-to-thickness ratio) $D/t \approx 4$, which is a typical average ratio for this kind of sample.$^{8,14}$ $C_B$ is the volume fraction of ferrimagnetic (blocked) particles. Within the framework of the ideal Stoner–Wohlfarth model, we should expect that

$$M_r/M_s = 0.5C_B,$$  

where $M_r$ is the remanent magnetization and 0.5 is the value of the $M_r/M_s$ ratio at $T = 0$ ($C_B = 1$, all particles blocked). It is clear from Fig. 8(a) that $M_r/M_s < 0.5$ as we approach $T \to 0$, which might be due to different facts, such as noncoherent rotational magnetization processes, interparticle interaction, magnetization reversal through tunneling, distribution of anisotropy fields, and particle size distribution. We may obtain an estimate of the fraction of blocked particles as a function of temperature from the expression

$$C_B(T) = (M_r/M_s)/(M_r/M_s)_{T \to 0},$$  

where $(M_r/M_s)_{T \to 0}$ is the value of the remanent-to-saturation ratio at $T \to 0$. As we cannot measure below 35 K since the sample is not saturated, we take $(M_r/M_s)_{T \to 0} \approx 0.3$ from the extrapolation of Fig. 8(a), as-
FIG. 8. (a) Remanent-to-saturation magnetization ratio as a function of temperature for the Co-Ti sample: (○) $M_r/M_s$, (□) $M(10\text{ Oe})/M_s$, and (*) $M(10\text{ Oe})/M_s(T=115\text{ K})$. (b) derivative of the same data with respect to temperature, as a function of temperature. Solid line corresponds to the best fit of the data to a lognormal distribution.

From these results, we understand that there is a large dead magnetic layer at particle surface, which behaves as paramagnetic and contributes to the high field differential susceptibility. Then, as experimental saturation magnetization (both $M_0$ and $M_s$) concern the whole particle (not only the inside core where magnetic structure is that of a bulk specimen, but also the dead magnetic layer), the volume of the magnetic unit must be related only to the inside core. This is the reason why we have used the experimental value of the zero-field saturation magnetization for microcrystalline particles $M_0^{\text{max}}$ ($M_0^{\text{max}}=90\text{ emu/g}$ at 4.2 K, Ref. 11) in the definition of both the first anisotropy constant $K_1$ and the shape anisotropy $H_{\text{sh}}$ ($K_1=1/2(H_kM_0^{\text{max}})$, $H_{\text{sh}}=\Delta N M_0^{\text{max}}$). In addition, we have introduced an effective anisotropy constant $K_{\text{eff}}$ in Eqs. (2)–(4), since in the present case the shape anisotropy is not negligible. $K_{\text{eff}}$ is related to the anisotropy field $H_a=H_k-H_{\text{sh}}$ through $K_{\text{eff}}=1/2(H_aM_0^{\text{max}})$.

We notice that we have checked the purity of the sample by different ways in order to exclude the presence of spurious phases that lead to a reduction of the experimental saturation magnetization. The Curie temperature has been obtained with a vibrating sample magnetometer (VSM). The experimental value ($T_c\approx 633\text{ K}$) is very close to the value obtained for microcrystalline powders. The evolution of the magnetization with temperature up to $T_c$ is regular and reversible, and no anomaly is observed, thus suggesting that other magnetic phases, if present, are below the detection limit of the apparatus. Moreover, the nucleation and growth of the ferrite phase have been followed carefully by chemical methods (thermogravimetry, kinetics), allowing to assert that the $M$-type phase is the major phase in the sample. Finally, although x-ray diffraction patterns have been also recorded, Bragg peaks are so broad that no conclusion concerning minor phases in the sample may be drawn from them.

The fitted magnetocrystalline anisotropy fields $H_k$ are about 23 kOe between 35 K and $\langle T_b \rangle$. The anisotropy fields $H_a$ are about 20 kOe in this temperature range. $H_a$ and $H_k$ are sensitive to the magnetic field interval where they are fitted. It is actually difficult to separate the $A/H$ term from the $B/H^2$ term when fitting experimental $M(H)$ curves to Eq. (6). Only with magnetic fields well above 2–3 times the anisotropy field (which are not achievable with our experimental setup) may we be sure that the magnetization curves are purely of the $1/H^2$-type. We have fitted experimental curves to the $1/H^2$ term within magnetic field ranges always above 10 kOe, by fixing the $1/H$ contribution fitted below 10 kOe. We have detected relative enhancements of the values given above which are always below 25%. The first anisotropy constant $K_1$ and the effective anisotropy constant $K_{\text{eff}}$ are about $5.5\times 10^6\text{ erg/cm}^3$ and $4.7\times 10^6\text{ erg/cm}^3$, respectively, between 35 K and $\langle T_b \rangle$, with a relative enhancement due to the fitting interval which is also below 25%.

All these results should be taken as approximate values for the following reasons: (i) the anisotropy fields derived from the law of approach saturation are overestimated in comparison with those obtained from other methods, such...

(a) 

(b)
as the singular point detection method (SPD) and the transverse susceptibility method, since we measure the larger values of the distribution of anisotropy fields \( g(H_a) \) instead of the mean value. (ii) superparamagnetic particles contribute to the law of approach saturation through the Langevin function \( L(x) = \coth(x) - 1/x \), with \( x = VM \mu H/(k_B T) \). \( L(x) \) is 1 - 1/x when x is large, and it is linear with x when x is small. As a result, the ratio \( VH/T \) determines if superparamagnetic particles contribute either to the 1/H term (and, therefore, this cannot be univocally attributed to crystal defects) or to the initial susceptibility \( \chi_{in} \). Also, at intermediate values of x, \( L(x) \) may cause some uncertainty in the determination of the anisotropy field. We notice that x is of the order of 2.3 when \( V = \langle V \rangle \), \( T = \langle T_B \rangle \) (see below) and \( H = 1000 \) Oe, if we use \( M_{\text{max}} \). (iii) as the sample is polycrystalline, we will have some scattering in the demagnetizing factor \( \Delta N \). (iv) it is difficult to separate the \( A/H \) from the \( B/H^2 \) contribution, in the considered magnetic field range. The determination of the anisotropy field from independent methods is in progress now.

The fitted magnetocrystalline anisotropy fields \( H_k \) are larger than that reported for microcrystalline particles of the pure BaFe\(_{12}\)O\(_{19}\) phase (about 17 kOe at 4.2 K), and for the Co-Ti \( x = 0.8 \) sample (about 13 kOe at 4.2 K, Ref. 11). Referring to the first anisotropy constant \( K_1 \), the fitted values are of the same order of magnitude as those reported for the pure phase (4.4 \( \times 10^6 \) erg/cm\(^3\) at 4.2 K and 3.2 \( \times 10^6 \) erg/cm\(^3\) at 300 K, Ref. 3) and are larger than those of the Co-Ti \( x = 0.8 \) compound (3 \( \times 10^6 \) erg/cm\(^3\) at 4.2 K (Ref. 11) and 1 \( \times 10^6 \) erg/cm\(^3\) at 300 K (Ref. 31)).

All these results suggest that surface effects are of the greatest importance for nanocrystalline M-type barium ferrite particles and they seem to indicate that when reducing particle size, \( M_0 \) strongly decreases and \( H_k \), \( K_1 \), and \( K_{\text{eff}} \) are enhanced with respect to the bulk values (\( K_1 \) and \( K_{\text{eff}} \) have been derived assuming that the inside core is responsible for the magnetic properties). Consequently, we suggest that the anisotropy comes from two different sources, one from the volume of the inside core and the other from the limit surface of this core. Therefore, the anisotropy constant \( K \) for nanocrystalline barium ferrite particles might be written as \( K = K_b + (S/V)K_x \), where \( K_b \) is the anisotropy constant corresponding to the bulk (in erg/cm\(^3\)), \( K_x \) is the anisotropy constant corresponding to the surface of the inside core (in erg/cm\(^2\)) and \( S \) is the limit surface of the inside core. According to this expression, \( K \) increases when particle size decreases.

The ratio \( H_a/H_b \) is expected to be 0.48 in the classical Stoner–Wohlfarth model of an array of randomly oriented single domain noninteracting ferro/ferrimagnetically monodisperse particles. In our case, this should be accomplished at the limit \( T \rightarrow 0 \), when all particles are blocked. However, \( H_a(0)/H_a(0) \) is of the order of 0.2-0.3, much smaller than the expected value, as we have already detected in the remanence-to-saturation ratio. The same reasons that in that case might account for this reduction. The ratio \( M_a/M_b \) is displayed in Fig. 8(a). From the derivative of \( M_a/M_b \) with respect to temperature we have extracted the distribution of blocking temperatures \( F(T_B) \) corresponding to the distribution of particle volumes \( f(V) \). We have fitted \( F(T_B) \) to lognormal distribution [Fig. 8(b)]

\[
F(T_B) = \frac{1}{\sqrt{2\pi\sigma T_B}} \exp\left[-\frac{1}{2}\sigma^2 \left(\frac{T_B}{T_B}\right)^2\right],
\]

where \( \ln(T_B) \) is the mean value of \( \ln(T_B) \) and \( \sigma \) is an adimensional parameter associated with the dispersion around \( \ln(T_B) \). The mean \( T_B \) value and its dispersion \( \sigma_T \) are written \( \langle T_B \rangle = T_B \exp(-\sigma_T^2) \) and \( \sigma_T = T_B \exp(-\sigma^2) \). Equation (10) and the experimental \( d(M_a/M_b)/dT vs T \) curve lead to \( \langle T_B \rangle = 81 \) K and \( \sigma_T = 40 \) K. Then, the maximum of the \( M_{\text{ZFC}}(T_B) \) and \( \langle T_B \rangle \) are related through \( T_B = c\langle T_B \rangle \) with \( c \approx 2.4 \), which represents about 20% excess with respect to the \( c = 2 \) value expected for a quasinormal distribution. We attribute this variation to the experimental error in the \( M_a/M_b \) data. Furthermore, Fig. 8(b) indicates that nearly all particles are superparamagnetic at room temperature, while all particles are blocked below about 20 K.

As the distribution of blocking temperatures \( F(T_B) \) and the distribution of particle volumes \( f(V) \) are related through Eq. (4), \( \langle T_B \rangle \) leads to a mean anisotropy energy \( \langle K_1 V \rangle \approx (2.8 \pm 1.4) \times 10^{-13} \) erg, which is in good agreement with the mean values 2.4 \( \times 10^{-13} \) erg and 2.1 \( \times 10^{-13} \) erg that we have derived from the \( H_a \) vs. \( T^{1/2} \) and \( H_a \) vs \( T^{1/4} \) curves, respectively. Taking the mean value of the effective anisotropy constant \( K_{\text{eff}} \) of about 4.7 \( \times 10^6 \) erg/cm\(^3\) (we neglect the distribution of anisotropy fields), the mean volume of the magnetic unit \( \langle V \rangle \) is \( (6 \pm 3) \times 10^3 \) A\(^3\), smaller than the mean particle volume obtained from TEM \( \langle V \rangle \approx 1.1 \times 10^5 \) A\(^3\), Ref. 16), as expected when there is a large dead magnetic layer at particle surface. We notice that this particle volume, together with \( D_{1/2} \approx 4 \), leads us to a specific surface area of about 271 m\(^2\)/g. Kubo et al. report that the saturation magnetization of some barium ferrite samples \( x = 0, 0.5, 0.85 \), with some particle sizes for each substitution significantly decreases when the surface specific area increases within 5 and 35 m\(^2\)/g. We believe that the extrapolation of this decrease fill the specific surface area of the sample may explain the saturation magnetization that we find experimentally.

IV. SUMMARY AND CONCLUSIONS

We have studied the static magnetic properties of three different M-type doped barium ferrite compounds prepared by the glass crystallization method.

The ZFC and FC curves of all samples display the typical features of a small particle system. The ZFC processes present a broad peak at a temperature \( T_M \), which depends on the particle size distribution. TEM shows that the larger the mean particle volume, the higher \( T_M \). There is also a clear irreversibility between the ZFC and FC curves, which tends to disappear as we approach the superparamagnetic region.

A wide magnetic characterization of the Co-Ti compound has been recorded. Saturation magnetization fol-
ollows a $T^{a}$-law above 120 K, with $a \approx 2.7$. We suggest that relaxation effects may preclude the observation of spins at low temperature waves, while we detect the characteristic contribution of interacting spins waves at high temperature. However, we notice that small particles present a particular contribution of interacting spins waves at high temperature. Moreover, we find that small particles present a particular contribution of interacting spins waves at high temperature.

Isothermal magnetization curves have been fitted to the LAS expressed in Eq. (6) below the mean blocking temperature $T_B$. The zero-field saturation magnetization $M_0$ is much smaller and the high-field differential susceptibility $\chi_d$ is much larger than the experimental values for microcrystalline particles. We ascribe this to finite-size effects. We understand that there is a large dead magnetic layer at particle surface. Furthermore, the anisotropy constant $K_1$ and the anisotropy field $H_K$, which we associated with the inside core of the particle where the magnetic structure is that of a bulk specimen, are larger than those reported for micromagnetic particles. We suggest that the anisotropy of nanocrystalline barium ferrite particles comes from both the volume and the limit surface of the inside core.

The distribution of blocking temperatures has been obtained from the derivative of remanent-to-saturation ratio with respect to temperature, which has been fitted to a lognormal distribution. We obtain that the mean blocking temperature $T_B$ is $(81 \pm 40)$ K, leading to a mean energy of anisotropy $\langle K_{eff} V \rangle = (2.8 \pm 1.4) \times 10^{-13}$ erg, in good agreement with mean values derived from $H_K$ vs $T^{a}$-laws. As the effective anisotropy constant $K_{eff}$ is about $4.7 \times 10^6$ erg/cm$^3$, the mean volume of the magnetic unit is $(6 \pm 3) \times 10^4$ $\AA^3$, smaller, as expected, than the mean particle volume $V \approx 1.1 \times 10^5$ $\AA^3$ obtained from TEM.

We conclude from our results that the GCM is successful in obtaining very small Co-Ti particles with a narrow distribution of sizes in comparison with microcrystalline powders. At present, dynamic magnetic measurements are being recorded. We are measuring the time dependence of the FC magnetization, and our main goals are to obtain some information about the energy barrier distribution and its dependence on the magnetic field and information about the relaxation mechanism as $T \to 0$.


16. P. Gürme and E. Sinn (private communication).


