

Static Magnetic Properties of Nanocrystalline Co-Ti Doped Barium Ferrite $\text{BaFe}_{12-2x}\text{Co}_x\text{Ti}_x\text{O}_{19}$ ($x = 0.8$)

X. Batlle, M. García del Muro and J. Tejada
 Departament de Física Fonamental, Universitat de Barcelona
 Diagonal 647, 08028-Barcelona, Catalonia, Spain

H. Pfeiffer, P. Görnert and E. Sinn
 Institut für Physikalische Hochtechnologie
 Helmholtzweg 4, O-6900, Jena, Germany

Abstract- We have studied the static magnetic properties of nanocrystalline Co-Ti doped barium ferrite $\text{BaFe}_{10.4}\text{Co}_{0.8}\text{Ti}_{0.8}\text{O}_{19}$. The zero-field-cooled (ZFC) and field-cooled (FC) processes show the typical features of a small particle system. The dependence on temperature of the coercive field is discussed within the scope of an aligned and random assembly of particles. The distribution of blocking temperatures is obtained from the remanent-to-saturation magnetization ratio, leading to the mean volume of the magnetic unit ($\approx(6 \pm 3) \cdot 10^4 \text{ \AA}^3$), in agreement with the mean particle volume determined by TEM ($\approx 1.1 \cdot 10^5 \text{ \AA}^3$). Remanence curves are used to derive the anisotropy field distribution and the interparticle magnetic interaction.

I. INTRODUCTION

M-type barium ferrite $\text{BaFe}_{12}\text{O}_{19}$ has been widely studied because of its applicability to high-density magnetic and magneto-optic recording media. $\text{BaFe}_{12}\text{O}_{19}$ is usually doped with Co^{2+} in order to reduce the magnetocrystalline anisotropy. The Co-Ti doping scheme and, in particular, the $\text{BaFe}_{10.4}\text{Co}_{0.8}\text{Ti}_{0.8}\text{O}_{19}$ sample, prove as the best substitution for magnetic recording applications [1]. Concerning synthesis procedures, the glass crystallization method (GCM) [2] allows to control both particle size and morphology. Within the nanocrystalline regime, GCM enables us to obtain powders with mean particle size ranging from about 80 Å to 300 Å, having a platelet-like shape and a narrow size distribution.

II. EXPERIMENTAL

The sample was prepared by GCM. This procedure is characterized by homogenized melt fluxes of Fe_2O_3 , BaO, B_2O_3 , TiO_2 and CoO at about 1300°C, which were amorphized by rapid quenching. Barium ferrite particles crystallized to suitable sizes by annealing the glass flakes above 550 °C. A detailed explanation on this treatment is given in [2]. Magnetization measurements were carried out with a SHE S.Q.U.I.D magnetometer on two different samples: (1) in the first sample the

powder was fixed with a glue in order to avoid particle rotation towards the field axis (fixed particles), and (2) in the second sample the powder was just placed in a plastic bag (free particles).

III. RESULTS AND DISCUSSION

A. Free Particles

The ZFC curve shows a wide maximum at $T_M \approx 195 \text{ K}$ (Fig. 1), thus suggesting a distribution of volumes $f(V)$ in the sample, leading to a distribution of blocking temperatures $F(T_B)$. T_M is related to the mean blocking temperature $\langle T_B \rangle$ through $f(V)$ (see below). The FC magnetization (Fig. 1) is always above the ZFC up to about room temperature, indicating that magnetic irreversibility disappears as we approach the superparamagnetic regime. Saturation magnetization at 50 kOe (Inset of Fig. 1) decreases with temperature above 35 K (whence a characteristic T^{-1} -law is followed), while it decreases below this temperature since we cannot rotate the magnetic moments of all blocked particles along the magnetic field axis.

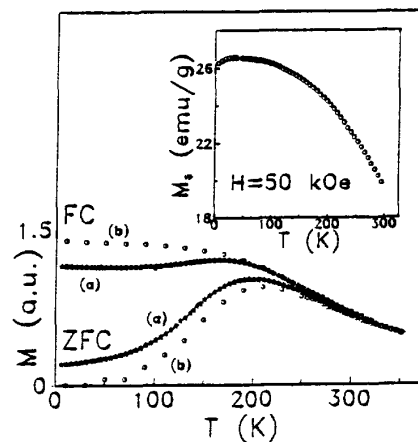


Fig. 1. ZFC and FC magnetizations measured at 35 Oe for (a) free particles and (b) fixed particles. Inset: Saturation magnetization M_s measured at 50 kOe for free particles.

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For mono-disperse, non interacting, ferro/ferrimagnetically ordered particles the the coercive field is expected to depend on temperature as $H_c = H_c(0) \cdot (1 - A \cdot T^k)$, with $A = (25 k_B / (K_{eff} \cdot V))^k$, and K_{eff} the effective anisotropy energy per unit volume. The k -exponent is $1/2$ for an assembly of aligned particles and 0.77 for an assembly of randomly oriented particles [3]. Both approaches lead us to similar close agreements with experimental results and they are followed up to 35 K, whence most of the particles are blocked (Fig. 2). We obtain that the mean anisotropy energy $\langle K_{eff} \cdot V \rangle$ is about $2.4 \cdot 10^{-13}$ erg for the aligned case and about $2.1 \cdot 10^{-13}$ erg for the random case.

Isothermal magnetization curves $M(H)$ were fitted to $M(H) = M_0 \cdot (1 - A/H - 1/15 \cdot (H_s/H)^2 \cdot C_B) + \chi_d \cdot H$, up to the mean blocking temperature $\langle T_B \rangle$ ($= 80$ K, see below). C_B stands for the fraction of ferromagnetic particles and may be obtained from $C_B = (M_r/M_s) / (M_r/M_s)_{T=0}$, M_r being the remanence and assuming $(M_r/M_s)_{T=0} \approx 0.3$, from the extrapolation of Fig. 3. C_B is larger than 0.5 below $\langle T_B \rangle$. H_a is the effective anisotropy field, defined as $H_a = H_k - H_{sh}$, H_k is the magnetocrystalline anisotropy field and H_{sh} is the shape anisotropy field. Zero field saturation magnetization M_0 (≈ 20 emu/g) is much smaller and high-field susceptibility χ_d ($\approx 10^{-4}$ emu/g) is much larger than those values corresponding to microscopic particles ($M_0^{max} \approx 90$ emu/g and $\chi_d^{min} \approx 10^{-5}$ emu/g at 4.2 K [1]), as a result of the enhancement of the finite-size effects. There is a large dead magnetic layer at particle surface which strongly modifies the magnetic parameters of nanocrystalline particles with respect to those of microcrystalline particles. The fitted anisotropy field H_a (≈ 20 kOe) and the effective anisotropy constant K_{eff} ($\approx 5 \cdot 10^6$ erg/cm³) are also larger than those of microcrystalline particles, due to the contribution of the surface. H_a and K_{eff} are related through $H_a = (2 \cdot K_{eff}) / M_0^{max}$, and they are constant, within the experimental error, from 35 K up to $\langle T_B \rangle = 80$ K.

We have also fitted the derivative of M_r/M_s with respect to temperature (Inset of Fig. 3) to a log-normal distribution [4], whence we extract $F(T_B)$, which is related to $f(V)$ through $\langle K_{eff} \cdot V \rangle \approx 25 \cdot k_B \cdot \langle T_B \rangle$. We obtain $\langle T_B \rangle = (80 \pm 40)$ K and $\langle K_{eff} \cdot V \rangle \approx 2.8 \cdot 10^{-13}$ erg, the latter in agreement with those derived from the H_c vs T^k -laws. The mean anisotropy energy leads to a mean volume of the magnetic unit of $(6 \pm 3) \cdot 10^4 \text{ \AA}^3$, smaller, as expected, than the mean particle volume obtained from TEM ($\approx 1.1 \cdot 10^5 \text{ \AA}^3$) [4]. Also, $T_M = c \cdot \langle T_B \rangle$, with $c \approx 2.4$, which represents a 20% excess with respect to the expected value for a quasi-normal distribution ($c = 2$) [4].

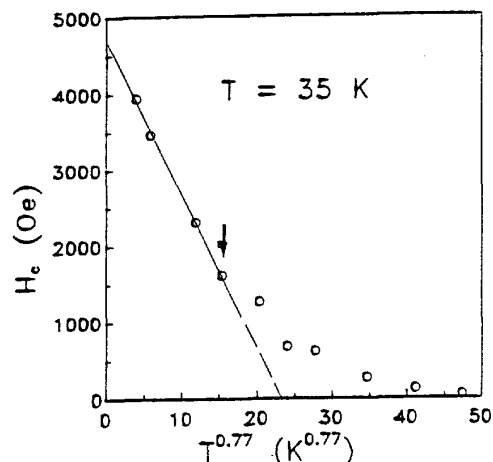


Fig. 2. Coercive field H_c plotted as a function of $T^{0.77}$ (random case) for free particles.

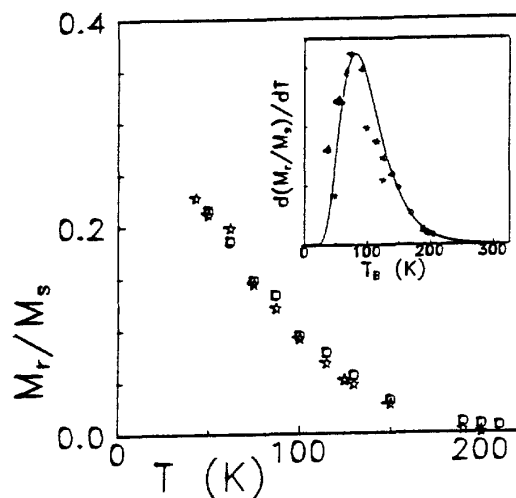


Fig. 3. Remanent-to-saturation magnetization ratio for free particles (\square) M_r/M_s , (\circ) $M(10 \text{ Oe})/M_s$, ($*$) $M(10 \text{ Oe})/M_s(115 \text{ K})$. Inset: derivative of the data with respect to temperature. Solid line corresponds to the best fit to a lognormal distribution of blocking temperatures.

B. Fixed Particles

The ZFC and FC processes of fixed particles are displayed in Fig. 1. Free and fixed particles tend to the same superparamagnetic regime at high temperatures, leading to an extrapolated ordering temperature of 220 K, indicating that interparticle interaction is ferromagnetic in the high temperature regime. The following differences are observed in the low temperature (blocked) regime: (i) the temperature of the ZFC maximum is slightly higher for fixed particles, since the thermal energy involved to make these particles superparamagnetic is higher, (ii) the ZFC of fixed particles is always below that of free particles, signaling a higher degree of random orientation of the easy axis of the

magnetization, and (iii) the FC of fixed particles is always above that of free particles, since the antiferromagnetic interparticle interaction in the blocked regime (as is shown below) allows free particles to arrange antiferromagnetically more easily than fixed particles.

Concerning the field dependence of the remanence curves, there are two different primary curves than can be measured: (1) the isothermal remanent magnetization $m_r(H) = M_r(H)/M_r(H_{max})$, which is obtained measuring the remanence from the initially demagnetized state by taking the sample through successive minor loops (Fig. 4), and from where we obtain the anisotropy field distribution $g(H_a)$ by differentiating $m_r(H)$ with respect to H (Inset of Fig. 4), and (2) the dc demagnetization remanence curve $m_d(H) = M_d(H)/M_d(H_{max})$ measuring the remanence by progressive demagnetization of a previously magnetized sample. Both curves $m_r(H)$ and $m_d(H)$ would lead to the same energy barrier distribution in a non-interacting system, which was expressed by Wohlfarth as $m_d(H) = 1 - 2 \cdot m_r(H)$. Deviations from linearity in the m_d vs m_r plot (Henkel plot) signal the existence of interparticle interaction, and may be monitored by representing $\Delta m = m_d(H) - (1 - 2 \cdot m_r(H))$ (Fig. 5). Δm gives a quantitative measure of the sign and strength of the interaction.

Neglecting the effect of thermal fluctuations due to superparamagnetic particles and assuming coherent rotation of the magnetization vector and non-interacting particles, the mean anisotropy field $\langle \overline{H}_a(T) \rangle$ may be calculated by $\langle \overline{H}_a(T) \rangle = 2 \cdot H_i$, whence H_i is the inflection point of $m_r(H)$ (Fig. 4 and inset), leading to $\langle \overline{H}_a(T) \rangle \approx 3.4$ kOe, 6.8 kOe and 14 kOe at 80 K, 43 K and 6 K, respectively. We note that the width of the anisotropy field distribution $g(H_a)$ strongly increases as we go down in temperature, and we assume that this is due to the fact that $g(H_a)$ cannot be calculated correctly in the high-field region at low temperatures since we cannot rotate the magnetic moments of all blocked particles. Pfeiffer et al. [3] proposed that the intrinsic mean value of the anisotropy field $\langle H_a(T) \rangle$ may be obtained by removing thermal fluctuations through $\langle H_a(T) \rangle = z \cdot \langle \overline{H}_a(T) \rangle$, being z the solution of the equation $(z-1)z^{0.3} = [(50 \text{ k}_B \cdot T)/(V(T) \cdot M_0^{max} \cdot \langle \overline{H}_a(T) \rangle)]^{0.7}$, leading to $\langle H_a(T) \rangle$ values of about 20 kOe, which are of the same order of magnitude as those derived from the law to approach saturation.

Finally, Fig. 5 evidences the antiferromagnetic ($\Delta m < 0$) interparticle interaction in the low temperature regime, which is in contrast with the ferromagnetic interparticle interaction in the high temperature regime. A detailed explanation on this fact is given in [3] and [5].

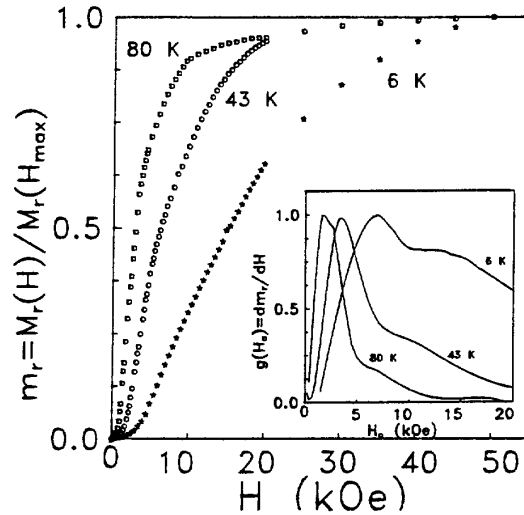


Fig. 4. Isothermal remanent magnetization $m_r(H)$ as a function of the applied magnetic field for fixed particles. Inset: derivative of $m_r(H)$ with respect to H , showing the anisotropy field distribution $g(H_a)$.

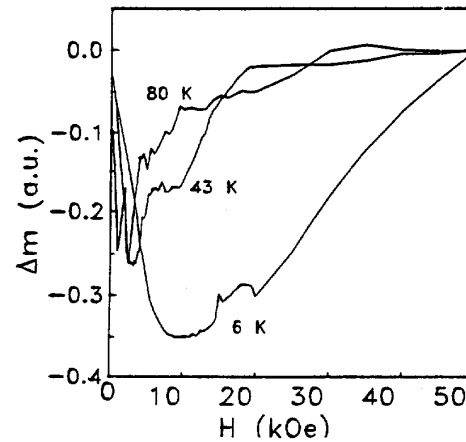


Fig. 5. Henkel plot (Δm vs H) for fixed particles, showing the antiferromagnetic ($\Delta m < 0$) interparticle interaction in the low temperature regime.

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