Supplementary Information

Exploring Reaction Conditions to Improve the Magnetic Response of Cobalt-Doped Ferrite Nanoparticles.

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**SUPPORTING INFORMATION**

**Model S1.** Effective anisotropy constant, $K_{eff}$, calculation within the Non-Interacting Super-Paramagnetic (SPM) model.

**Model S2.** Determination of Anisotropy Constant.

**Figure S1.** X-Ray diffraction pattern of the residue of the Co0.15_60 sample obtained after the thermogravimetric analysis.

**Figure S2.** Particle size distributions of Co0.15_30, Co0.15_45, Co0.15_60, Co0.10_60, Co0.04_60, Co0.01_60, Co0.15_75, Co0.15_90, Co0.15_105 and Co0.15_120.

**Figure S3.** Magnetic susceptibility ($\chi_{\text{ZFC}}$ and $\chi_{\text{FC}}$) measured at 10 Oe and derivative $-d(\chi_{\text{FC}}-\chi_{\text{ZFC}})/dT$ of (a) Co0.15_30, (b)Co0.15_45, (c)Co0.15_60, (d)Co0.15_75, (e)Co0.15_90, (f)Co0.15_10, (g)Co0.15_120, (h)Co0.04_60, (i)Co0.01_60 and (j)Co0.10_60.

**Figure S4.** Hysteresis loops at 5 K for the samples obtained with different reflux times (left) and Co contents (right).
Model S1. Effective anisotropy constant, $K_{\text{eff}}$, calculation within the Non-Interacting Super-Paramagnetic (SPM) model.

In a set of uniaxial magnetic single domains of size $D$ oriented at random, neglecting the dipolar interaction, the effective anisotropy constant is proportional to the so-called blocking temperature ($T_B$):

$$ K_{\text{eff}} = \frac{k_B \ln(\tau_m / \tau_0)}{V} T_B $$

(1)

$T_B$ becomes a direct experimental measurement of the energy barrier between the two ground states “up” and “down” of the particle magnetic moment ($K_V$). In equation (1), $\tau_m$ is the characteristic time of the experiment (time window) and $\tau_0$ is the inverse of the natural fluctuation rate of the particle magnetic moment.

In a measurement of DC magnetization $\ln(\tau_m / \tau_0) \approx 25$, so it follows that, assuming a set of particles of identical size, the effective anisotropy constant can be directly deduced from $T_B$ as:

$$ K_{\text{eff}} = \frac{25k_B}{V} T_B $$

(2)

In such an ideal system, $T_B$ coincides exactly with the maximum of the ZFC curve. When the natural dispersion of sizes is taken into account, equation (2) turns into the following one:

$$ K_{\text{eff}} = \frac{25k_B}{V} \langle T_B \rangle $$

(3)

where $\langle T_B \rangle$ is the average of the blocking temperatures of the population, each one depending on the size of a given particle. It is to note that $\langle T_B \rangle$ does not lie at the maximum of the ZFC, in a set of particles with some dispersity.

In order to calculate the average blocking temperature, determination of the $f(T_B)$ (proportional to the energy barrier distribution) is necessary. It can be obtained experimentally from the ZFC/FC measurement of magnetization under a sufficiently small-applied field, considering that:

$$ f(T_B) \approx \frac{d}{dT}(M_{FC} - M_{ZFC}) $$

(4)

In this way and after normalizing the derivative of the difference between ZFC and FC with the condition: $\int_0^{T_B} f(T_B) dT_B = 1$, the average blocking temperature is given by:

$$ \langle T_B \rangle = \int_0^{T_B} f(T_B) dT_B $$

(5)
**Model S2.** Determination of Anisotropy Constant.

**Fit of ZFC/FC measurements**

A simple non-interacting model has been used for the fit, in which the population of MNPs (given by a size distribution \( f(D) \)) is sharply divided in two groups at each temperature, depending on their particular size: the fraction in an ideal superparamagnetic state that corresponds to MNPs below a certain critical volume and those, above such limit, whose super spin remains blocked:

\[
M_{ZFC}(T) = \int_{0}^{V_c} M_{S}(\frac{MV_{C}}{k_{B}T})f(D)dV + M_{S}(\frac{MV_{C}}{3K_{C}})f(V)\mathrm{d}V
\]  

(6)

In the first term, we make use of the low energy barrier approximation where the energy barrier (defined as \( K_{eff}V \), being \( V \) the particle volume) is much smaller than the thermal energy \( (k_{B}T) \) and so can be omitted. Accordingly, the response of the magnetization to changes of magnetic field or temperature (\( H \) or \( T \)) follows a Langevin function, where \( M \) is the particle magnetization (A/m in S.I.) and \( M_{S} \) is the experimental saturation magnetization (including non-magnetic mass contribution, in general). Both the experimental magnetization and the particle magnetization are allowed to decrease with temperature following a spin wave-like behavior (Bloch type law) as:

\[
M(T) = M(0)e^{-BT^{3/2}}
\]

(7)

where the so-called Bloch constant \( (B) \) has been obtained from the magnetization measurements as a function of temperature under the maximum field of 7T, being between 2 and \( 4 \times 10^{-5} \) in all cases.

The second term component results from the initial susceptibility of a randomly oriented magnetic domains either with uniaxial \( (K_{U}) \) or with cubic anisotropy \( (K_{C}) \) provided that \( K_{C} > 0 \). Note that \( K_{C} \) is the first cubic anisotropy and is equal to \( 4K_{eff} \) if \( K_{C} > 0 \) as in Co ferrite. The threshold between the two populations (it is limiting both integrals) is given by a critical diameter or volume \( (D_{C}/D_{U}) \) such that:

\[
V_{C}(T) = \frac{25k_{B}T}{K_{eff}(T)}
\]

(8)

In this model, the position and shape of the ZFC maximum depends on the anisotropy through this critical volume that depends explicitly on temperature and also implicitly, through the function \( K_{eff}(T) \) which is given by different models as stated in the manuscript, depending on the relative content of Co ferrite.
Figure S1. X-Ray diffraction pattern of the residue of the Co_{0.15}_60 sample obtained after the thermogravimetric analysis
Figure S2. Particle size distributions of Co_{0.15}_30, Co_{0.15}_45, Co_{0.15}_60, Co_{0.10}_60, Co_{0.04}_60, Co_{0.01}_60, Co_{0.15}_75, Co_{0.15}_90, Co_{0.15}_105 and Co_{0.15}_120.
Figure S3. Magnetic susceptibility (ZFC and FC) measured at 10 Oe and derivative $-d(\chi_{\text{FC}}-\chi_{\text{ZFC}})/dT$ of (a) Co$_{0.15}$ \_30, (b) Co$_{0.15}$ \_45, (c) Co$_{0.15}$ \_60, (d) Co$_{0.15}$ \_75, (e) Co$_{0.15}$ \_90, (f) Co$_{0.15}$ \_105 and (g) Co$_{0.15}$ \_120.
Figure S3 (continued). Magnetic susceptibility (ZFC and FC) measured at 10 Oe and derivative $-d(\chi_{FC}-\chi_{ZFC})/dT$ of (a) $\text{Co}_{0.10}\_60$, (b) $\text{Co}_{0.04}\_60$ and (c) $\text{Co}_{0.01}\_60$. 
Figure S4. Hysteresis loops at 5 K for the samples obtained with different reflux times (left) and Co contents (right).

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