

# Preparation and Magnetic Study of the $\text{CoFe}_2\text{O}_4$ – $\text{CoFe}_2$ Nanocomposite Powders

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Ferri-ferromagnetic nanocomposites  $\text{CoFe}_2\text{O}_4$ – $\text{CoFe}_2$  were prepared via reduction of the cobalt ferrite  $\text{CoFe}_2\text{O}_4$  into a hydrogen atmosphere and by heat treatments. This preparation method yielded powders with relative volume fraction of  $\text{CoFe}_2\text{O}_4$  and  $\text{CoFe}_2$  in the range 0–0.91. The structure and the room temperature magnetization of the samples were analyzed by X-ray diffraction, scanning electron microscope (SEM) and transmission electron microscope (TEM), and by vibrating sample magnetometry, respectively. It was found that the saturation magnetization of the nanocomposite powders increases with the volume fraction of the ferromagnetic phase while their coercivity decreases. The highest value (5 kJ/m<sup>3</sup>) for the maximum energy product  $(BH)_{\text{max}}$  was obtained for the sample containing 91% in volume of  $\text{CoFe}_2$ . This  $(BH)_{\text{max}}$  is 19% higher than the value measured in pure  $\text{CoFe}_2\text{O}_4$ . The magnetic field dependence of the magnetization did also behave as the nanocomposite powders were single-phase materials. This result indicates that the hard ferrimagnet  $\text{CoFe}_2\text{O}_4$  and the soft ferromagnet  $\text{CoFe}_2$  are effectively exchange coupled and that their magnetization reverses cooperatively in the range of compositions investigated.

**Index Terms**—Cobalt ferrites, exchange coupling, nanocomposite material.

## I. INTRODUCTION

AN important goal in material science is to develop new materials at the nanometric scale. This class of materials becomes particularly important because its physical properties change dramatically with the size and with the local structure of the grains. These discoveries strongly influenced fields such as catalysis, magnetism, optoelectronics and medicine [1]–[3]. Nanoparticulate powders of the oxide cobalt ferrite  $\text{CoFe}_2\text{O}_4$ , on one side, become an important magnetic material because of their potential application in ferrofluids, in magnetic fluids, in magnetic recording media, and in resonance imaging. It presents high magnetocrystalline anisotropy, moderate saturation magnetization, remarkable chemical stability, and mechanical hardness [4], [5]. The metallic ferromagnet  $\text{CoFe}_2$ , on the other side, is a soft-magnetic material with unique magnetic properties. Among them are a large magnetic permeability and a very high saturation magnetization (above 230 emu/g). For these reasons and due to the great potential use in developing new magnetoresistive devices [6], the nanocomposites  $\text{CoFe}_2\text{O}_4$ – $\text{CoFe}_2$  are attracting great attention. Besides, they are a suitable system to be used to investigate the phenomenon of the exchange coupling in soft–hard ferri–ferromagnet composite material. This kind of composite materials is less studied and the exchange coupling itself is not completely elucidated yet. It is expected that the magnetic moments of  $\text{CoFe}_2\text{O}_4$  and  $\text{CoFe}_2$  couple with each other through the atomic layers of their interface. It is also expected that the exchange-spring mechanism would allow one to obtain hard magnetic nanocomposite materials that combine the high magnetic anisotropy property of one of the materials with

the high magnetization of the other. This, for instance, would allow to enhance the maximum energy product  $(BH)_{\text{max}}$  [7].

In this work, the magnetic properties of nanocomposite particles systems are reported. The nanoparticles are composed of ferrite cobalt  $\text{CoFe}_2\text{O}_4$  and ferromagnet  $\text{CoFe}_2$ . Samples with different relative volume fraction were obtained via heat treatments of the ferrite cobalt into a hydrogen flux. This is a very good procedure because it allows one to get the  $\text{CoFe}_2$  phase by starting from the single phase  $\text{CoFe}_2\text{O}_4$  cobalt ferrite following a simple and well-controlled route. It was possible to obtain a stepwise increase in the relative phase composition up to 91% in volume of  $\text{CoFe}_2$ . Within the range of volume fraction investigated, it was observed that the field dependence of the magnetization behaved as the samples were single phase-like. This result suggests that the magnetic phases in these materials are effectively exchange coupled and that the magnetization of both phases reverses cooperatively.

## II. EXPERIMENTAL PROCEDURE

Nanoparticles of pure  $\text{CoFe}_2\text{O}_4$  were produced using an ionic coordination (ICR) technique. First, the start solution was prepared from an aqueous solution of Fe and Co nitrites and from a chitosan solution mixture. Next, the solution was burned in an ambient atmosphere for 4 h at a temperature of 300 °C. Finally, the obtained powder was reduced at 300 °C under a hydrogen flux for various period of time (15, 30, 60, 90, and 120 min). This procedure yielded the nanocomposite  $\text{CoFe}_2\text{O}_4$ – $\text{CoFe}_2$  with different relative volumetric fraction (0.22, 0.40, 0.52, 0.73, and 0.91, respectively). The structural characterization was made up by X-ray diffraction (XRD) technique using the Cu–K $\alpha$  radiation and by scanning electron microscope (SEM) and transmission electron microscope (TEM). The magnetic properties

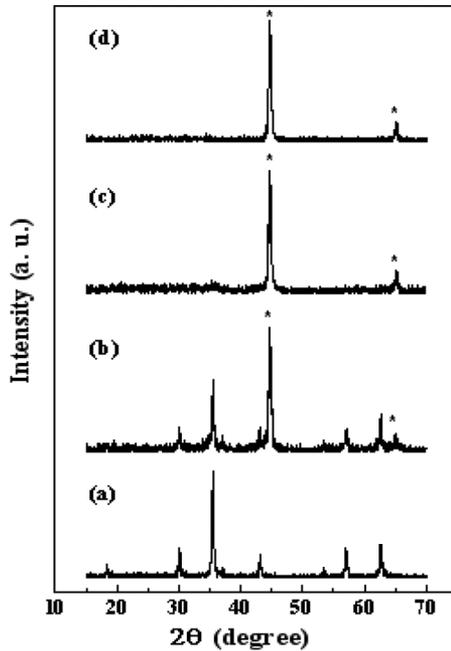


Fig. 1. X-ray diffractograms for the  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposite powders for representative values of the volume fraction  $f_V$ : (a) single-phase ( $f_V := 0$ )  $\text{CoFe}_2\text{O}_4$ , (b)  $f_V := 0.52$ , (c)  $f_V := 0.73$ , and (d)  $f_V := 0.91$ . The peaks marked with asterisks correspond to the  $\text{CoFe}_2$  phase.

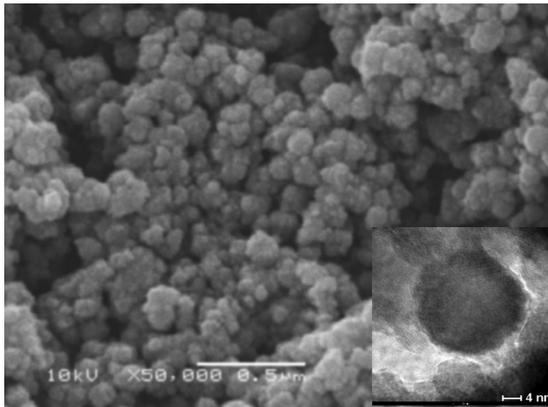


Fig. 2. SEM image for the pure  $\text{CoFe}_2\text{O}_4$  powder sample. The inset is a high-resolution TEM image for a nanoparticle of the sample with  $f_V = 0.40$ .

of the samples were measured using a vibrant sample magnetometer (VSM). The powders used in the magnetic measurements were compressed in a cylindrical glass sample holder. Each randomly packed polycrystalline grains contains a larger number of nanoparticles, yielding an overall random anisotropy system.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD data for four samples. In Fig. 1(a), the XRD for  $\text{CoFe}_2\text{O}_4$  as prepared by the ICR technique. It can be observed that this cobalt ferrite powder presents a high degree of crystallization and it is a single-phase one. Using the width of the most intense peaks, and their corresponding angles, the average particle size  $d$  was calculated using the Scherrer's formula. A  $d$  of about  $30.5 \pm 1.0$  nm for all the samples investigated was found out. The Rietveld refinement was also used to obtain

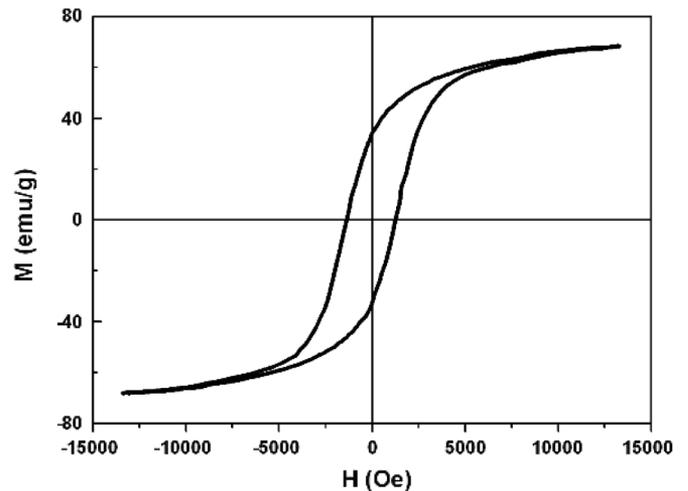


Fig. 3. Room temperature hysteresis loop for the single-phase  $\text{CoFe}_2\text{O}_4$  powder used to obtain the nanocomposites  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$ .

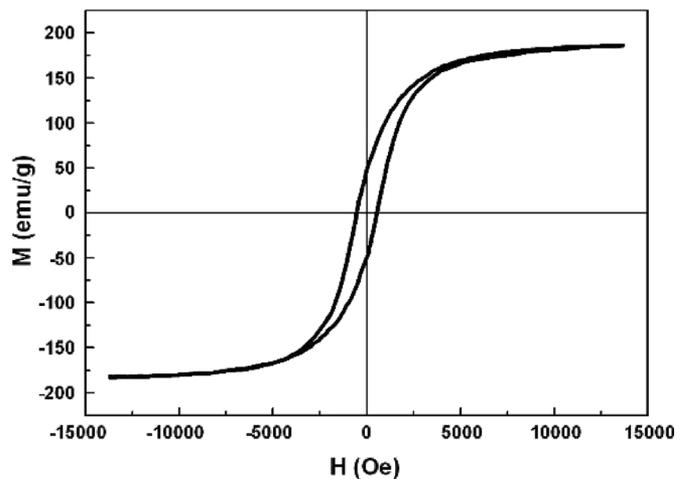


Fig. 4. Room temperature hysteresis loop for the  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposite powder with  $f_V = 0.91$ .

the average size particles yielding a  $d$  value very close to the one calculated by the Scherrer's formula. Fig. 1(b) shows the XRD data for the nanocomposite powder with a volume fraction  $f_V$  of  $\text{CoFe}_2$  of 0.52. It can be observed from this diffractogram that the peaks of both cobalt ferrite and of  $\text{CoFe}_2$  (marked with asterisks) are clearly seen. Fig. 1(d) shows the XRD of the nanocomposite with  $f_V = 0.91$ . For this sample composition, large peaks for the  $\text{CoFe}_2$  phase are seen, while the ones for the cobalt ferrite are almost imperceptible if compared, for instance, with those in Fig. 1(c) where  $f_v = 0.73$ . The aforementioned volume fractions were calculated by weighting the samples before and after the heat treatments into the hydrogen flux. The amount of the  $\text{CoFe}_2$  is calculated taking in consideration that the reduction reaction essentially removes four oxygens from the cobalt ferrite. The Rietveld refinement was also carried out in order to confirm the volume fractions. The X-ray data by itself revealed that the reduction reaction of the cobalt ferrite by hydrogen is an efficient method to obtain  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposites.

SEM and high-resolution TEM images for the starting powder and for a nanoparticle of a sample with  $f_V = 0.40$

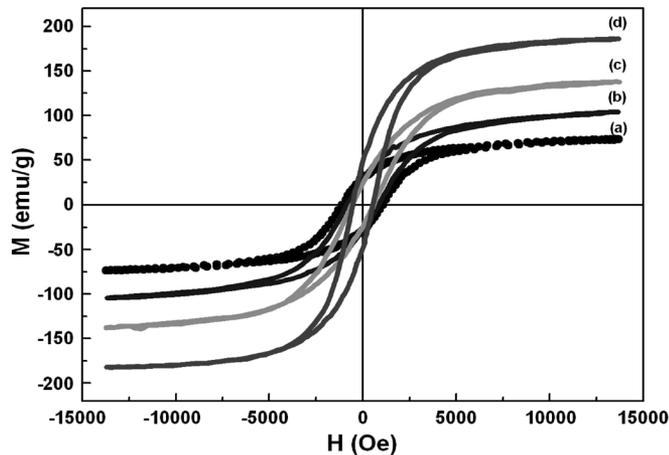


Fig. 5. Room temperature hysteresis curves for the  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposite powder samples with different volume fraction  $f_V$  of  $\text{CoFe}_2$ : (a)  $f_V := 0$ , (b)  $f_V := 0.52$ , (c)  $f_V := 0.73$ , and (d)  $f_V := 0.91$ .

(inset) are shown in Fig. 2. It is interesting to notice the small grain size distribution and the core-shell shape of the nanoparticle.

Fig. 3 shows a room temperature hysteresis loop for the pure cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) used to obtain the  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposite samples. The coercivity determined from this magnetization data was 1.32 kOe while the saturation ( $M_s$ ) and the remanent ( $M_r$ ) magnetizations were 68.0 and 33.7 emu/g, respectively. This magnetization value yields a magnetization ratio ( $M_r/M_s$ ) of 0.5. Fig. 4 shows the magnetic hysteresis loop for the nanocomposite powder sample with  $f_V = 0.91$ . For this sample, a coercivity of 539 Oe, saturation and remanent magnetizations of 184.3 and 49.4 emu/g, respectively, and a maximum energy product of 5 kJ/m<sup>3</sup> were found. This  $(BH)_{\text{max}}$  value is 19% higher than the one obtained for the pure cobalt ferrite phase [see Fig. 7(b)]. For comparison, hysteresis loops for samples with different volume fractions of  $\text{CoFe}_2$  are shown in Fig. 5. It can be observed from these curves that while  $M_s$  increases, the corresponding  $H_c$  decreases as long as the amount of the magnetically soft phase in the nanocomposites is increased. A reduction in  $H_c$  is a somewhat expected result because the size of the core (hard phase) is diminishing.

It is also interesting to notice at this point that the hysteresis loops shown in Figs. 4 and 5 are hysteresis loops of a two-phase system consisting of magnetically hard ( $\text{CoFe}_2\text{O}_4$ ) and soft ( $\text{CoFe}_2$ ) phases. Even so, the nanocomposite powder samples behave as if they were single-phase materials. Moreover, an enhancement in the  $(BH)_{\text{max}}$  for the nanocomposite powder with  $f_V = 0.91$  was observed. These overall results suggest that the two phases are effectively exchange coupled and that the magnetization of both phases reverses cooperatively.

Figs. 6 and 7 show the dependence of some magnetic parameters with the volume fraction  $f_V$  of  $\text{CoFe}_2$  in the nanocomposite powder samples. In Fig. 6(a), it is shown that  $M_s$  increases with the increment in the amount of the magnetically soft phase. This is a somewhat expected result because the high saturation magnetization of  $\text{CoFe}_2$ . Fig. 6(b) shows the corresponding variation of the magnetization ratio  $M_r/M_s$ . The  $M_r/M_s$  ratio decreases with increasing  $f_V$  showing an interesting upturn close

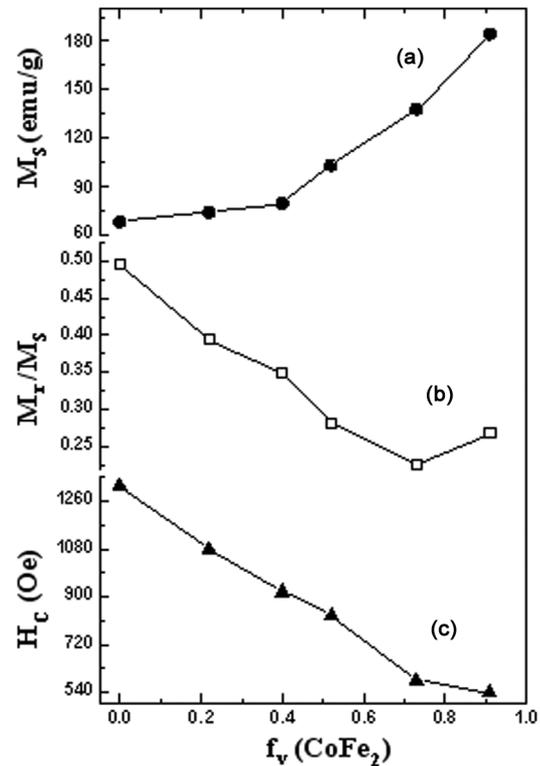


Fig. 6. Magnetic properties as a function of the volume fraction  $f_V$  of  $\text{CoFe}_2$  in the  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposites. (a) Saturation magnetization. (b) Magnetization ratio. (c) Coercive field.

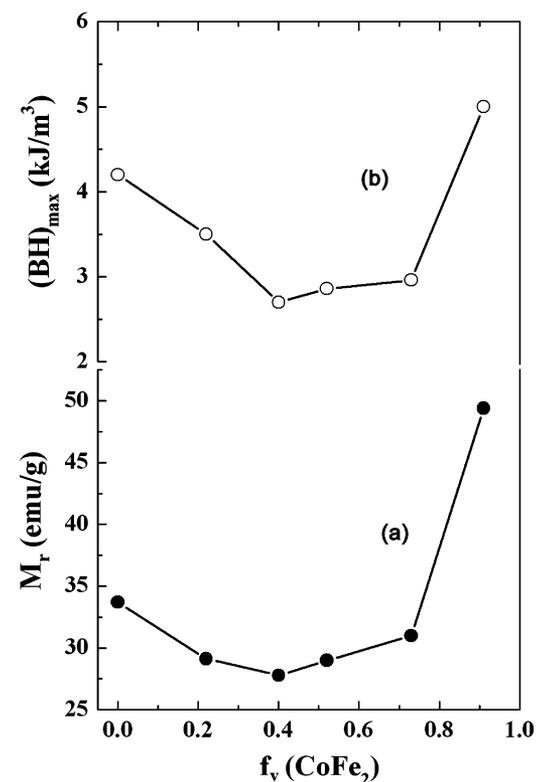


Fig. 7. Magnetic properties as a function of the volume fraction  $f_V$  of  $\text{CoFe}_2$  in the  $\text{CoFe}_2\text{O}_4\text{-CoFe}_2$  nanocomposite powder. (a) Remanent magnetization. (b) Maximum energy product.

to  $f_V = 0.73$  despite the continuous growth in  $M_s$ . Some observed trends were discussed in earlier published works performed on nanocomposite made of isotropic permanent magnets [8], [9], [12] and on theoretical studies based on micromagnetic simulation [10], [11]. The decreasing in the  $M_r/M_s$  ratio was attributed to the long-range dipolar interaction and to the appearance of a magnetic vortex state [11]. Fig. 6(c) shows the dependence of  $H_c$  on  $f_V$ . As can be seen,  $H_c$  decreases monotonically with the increase of  $f_V$ . It is also seen that close to  $f_V = 0.73$  there is a change in the way  $H_c$  diminishes. Therefore, due to the small nucleation field of the soft phase, large amounts of  $\text{CoFe}_2$  favor the nucleation of reverse domain in the nanocomposites. Figs. 7(a) and (b) shows the dependence of the remanent magnetization  $M_r$  and maximum energy product  $(BH)_{\max}$  with  $f_V$ . The behaviors of both curves are quite similar. They show a minimum close to  $f_V = 0.40$  and a sudden increase in both  $M_r$  and  $(BH)_{\max}$  above  $f_V = 0.91$ . The maximum energy product  $(BH)_{\max}$  [Fig. 7(b)] obtained for the nanocomposite with  $f_V = 0.91$  was  $5 \text{ kJ/m}^3$ , which is 19% higher than the one for pure cobalt ferrite ( $4.2 \text{ kJ/m}^3$ ). The remanence [Fig. 7(a)] increases from  $33.7 \text{ emu/g}$  for pure  $\text{CoFe}_2\text{O}_4$  to  $49.3 \text{ emu/g}$  for the nanocomposite with 91% in volume of the magnetically soft phase  $\text{CoFe}_2$ . Theoretical studying suggested that for the magnetic exchange-spring mechanism to take place on hard-soft magnetic nanocomposites about 10% in volume of the hard phase is required [7], [11]. It was also estimated that the critical sizes for the hard ( $b_k$ ) and for the soft ( $b_m$ ) phases required for the exchange spring to take place are both close to 5 nm. By assuming that the nanoparticles we are investigating are nearly spherical core shells, one can estimate the critical size for the sample with  $f_V = 0.91$ . Within this rough approximation, one finds  $2b_k = d(1 - f_V)^{1/3}$  and  $2b_m = d - 2b_k$ . Using  $d = 30.5 \text{ nm}$  and  $f_V = 0.91$ , one gets  $b_k = 6.8 \text{ nm}$  and  $b_m = 8.4 \text{ nm}$  whose values are very close to the estimated value (5 nm). Performing the same calculation for the sample with  $f_V = 0.40$ , one gets  $2b_k = 25.7 \text{ nm}$ . This value is very close to the diameter of the core showed in Fig. 2, which is approximately 24 nm. We also used the XRD to estimate the average diameter of the core ( $d_k = 2b_k$ ). The refinements yielded an average diameter of 10.6 nm, which again gives a  $b_k = 5.3 \text{ nm}$  close to the value predicted (5 nm) and to the estimated one (6.8 nm) using the spherical core-shell approximation. These results also support that the magnetic exchange-spring mechanism is present on the nanocomposite powder samples of  $\text{CoFe}_2\text{O}_4$ - $\text{CoFe}_2$  investigated in this work.

#### IV. CONCLUSION

Samples of the nanocomposite  $\text{CoFe}_2\text{O}_4$ - $\text{CoFe}_2$  were prepared by a reduction reaction of  $\text{CoFe}_2\text{O}_4$  into a hydrogen flux for a broad range of volume fraction of  $\text{CoFe}_2$ . This preparation method is very efficient. It requires low temperatures for heat

treatments and reasonable periods of time and it allows one to produce large amounts of sample materials. The magnetic parameters can be tuned by the time used in the sample preparation, for instance. In the range of volume fraction investigated, the nanocomposites behaved magnetically as being a single-phase-like material. The maximum product energy  $(BH)_{\max}$  for the nanocomposite with 91% in volume of  $\text{CoFe}_2$  was found to be 19% higher than the value obtained for the pure cobalt ferrite nanoparticles. The saturation magnetization increases about 31% for this composition. The overall results indicated that the ferrimagnetic  $\text{CoFe}_2\text{O}_4$  and the ferromagnetic  $\text{CoFe}_2$  are effectively exchange coupled and that the magnetization of both  $\text{CoFe}_2\text{O}_4$  and  $\text{CoFe}_2$  reverses cooperatively.

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