



Surfaces and local anisotropy effect in the magnetic order of Fe–Co–B nanoparticles

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Abstract

3 nm $(\text{Fe}_x\text{Co}_{1-x})_y\text{B}_{1-y}$ ($0 \leq x \leq 1$, $y \approx 0.6$) nanoparticles were synthesized by chemical route. XDR and TEM measurement show the amorphous nature of the samples. Size distribution was characterized by light-scattering measurement. Magnetization vs. magnetic field measurements at room temperature show hysteresis loop for all compositions, typical of blocked single domains. In powder samples, room temperature coercive field and remanent are larger for Fe- or Co-rich composition, and saturation magnetization exhibit a minimum at $x = 0.15$. This behaviour is related to the composition of the different local anisotropy associated to Fe and Co ions.

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Magnetism of fine particles has generated increasing interest due to their magnetic properties as well as their technological applications [1,2]. The effect of nanoscale confinement originates unusual magnetic behaviour, which may strongly differ from the one observed on conventional bulk materials in several aspects. As the particle size decreases, finite-size effects dominate the magnetic properties of fine particles due to surface effects

for example, in a particle of radius ~ 3 nm, about 70% of atoms lie on the surface) [3]. The picture of a magnetic single-domain particle where all spins are pointing in the same direction, thus leading to coherent relaxation process, is no longer valid if one considers the effect on the global magnetic properties of the particle of misaligned spins on the surface. It is expected that the decrease in the coordination number induces a weakening in the exchange interactions of the surface atoms with the surrounding ones. Also surface anisotropy may produce a disordered layer in the particle surface [4,5]. The effect of interparticle interactions

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is a complex problem. If the particles are very distant from each other, their dipole–dipole interactions are negligible. Magnetic interactions among particles can also modify the surface configuration of spins. In several cases, where strong interparticle interactions are present, a glass collective state has been observed [6]. In this context, amorphous nanoparticles deserve particular attention because the absence of crystalline anisotropy can lead to a more disordered state in the particle surface.

In this work we study the magnetic properties of $(\text{Fe}_x\text{Co}_{1-x})_y\text{B}_{1-y}$ amorphous nanoparticles with $0 \leq x \leq 1$ at room temperature.

Amorphous nanoparticles of Fe–Co–B alloy were obtained by reduction of aqueous solutions of metallic salts of CoSO_4 and FeSO_4 with a NaBH_4 solution [5,7]. The reduction was performed in an inert atmosphere by adding the metal ion solution drop-by-drop to the NaBH_4 one. A black powder was collected and washed with distilled water to remove residual ions, and then it was rinsed with acetone to remove water and finally dried in vacuum. Since the particles are strongly pyrophoric, a passivation with air was performed. The relative Fe/Co composition was determined by energy-dispersive spectroscopy microanalysis (EDX) and the boron concentration by atomic absorption analysis. The iron–cobalt ratio resulted close to the nominal one, the boron concentration was 40 at%. The X-ray powder diffraction pattern showed a broad spectrum confirming the amorphous nature of the particles (Fig. 1). The mean diameter and the size distribution were determined by TEM and light-scattering experiments. In Fig. 2, we show a TEM image of the $(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.6}\text{B}_{0.4}$ sample. The low contrast is due to the aggregate state of the sample and to its amorphous state. The mean diameter was ~ 3 nm and the distribution was determined by light-scattering method of an aqueous suspension of the particles. This method yields a narrow log-normal distribution centered at $\langle \phi \rangle = 2.8$ nm and a dispersion $\sigma = 1$ nm.

As the nanoparticles are ferromagnetically ordered, single-domain behaviour is expected to be observed. Magnetization measurements were performed as a function of the magnetic field up to

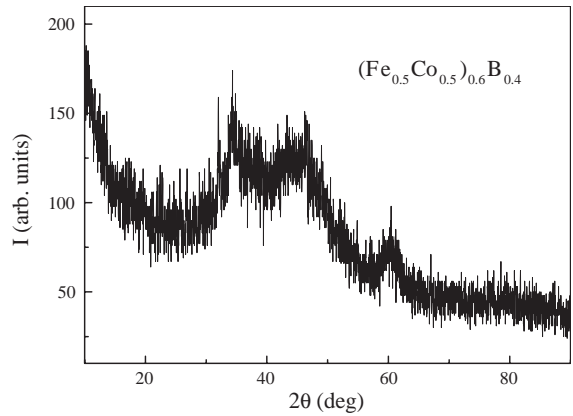


Fig. 1. X-ray powder diffraction pattern (Cu- K_α radiation) of the $(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.6}\text{B}_{0.4}$ sample.

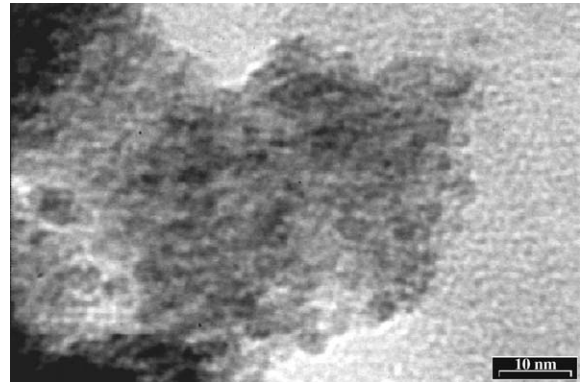


Fig. 2. Bright field TEM image of $(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.6}\text{B}_{0.4}$.

10 kOe at room temperature in a commercial VSM. For all compositions, a hysteresis appears as is shown in Fig. 3 for $x = 0.75$ and 0.50 samples. In Fig. 4 we have plotted the saturation magnetization, normalized remanence magnetization and the coercive field as a function of Fe composition. It is clear that the saturation magnetization, i.e. the magnetic moment of the particle, decreases with cobalt substitution. This change in the magnetic moment is not due exclusively to the different magnetic moment values for Fe and Co. In Fig. 4a we have plotted the line that corresponds to the saturation of each sample if the variation comes only from the dilution effect. In order to interpret the loss of

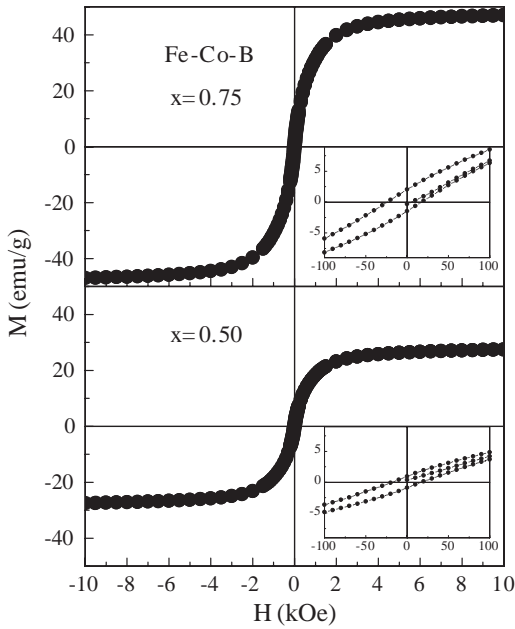


Fig. 3. Hysteresis loops taken at room temperature for two compositions.

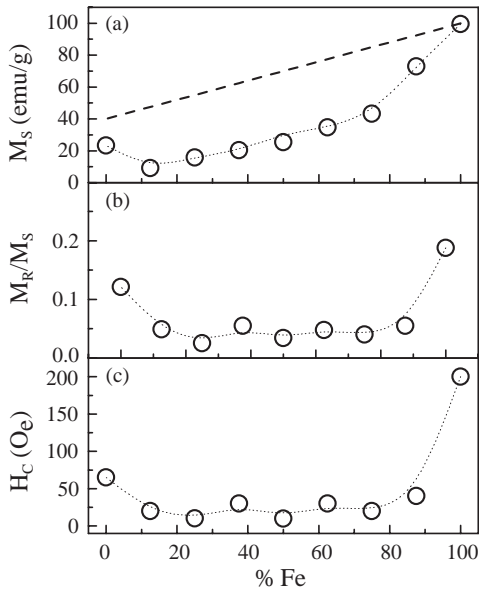


Fig. 4. (a) Saturation magnetization (the dashed line corresponds to variation considering the dilution effect, see text), (b) normalized remanence, and (c) coercive field as a function of composition. The dotted lines are only a guide to the eyes.

the magnetic moment, it is necessary to consider to core-shell structure of the internal ferromagnetic order of the particle. As is showed in previous experimental and theoretical works [4,5,8,9], surface iron spins have a surface anisotropy with the easy axis perpendicular to the particle surface. Contrarily, the surface cobalt spins have their easy axis parallel to the particle surface. Then, the ferromagnetic order of the shell layer of the particle depends on the exchange interaction and the local anisotropy, which tends to align the spins not even in the core ferromagnetic direction. If the particle has in the surface both species of spins, surface anisotropy of iron and cobalt competes between frustrating the magnetic order. Then, saturation magnetization decreases as is observed in our measurements. Remanence magnetization and coercive field follows the same behaviour. In particular, this frustration in the magnetic order and in the surface anisotropy reduces the total anisotropy of the particle decreasing the coercive field. It is noticeable that the coercive field has the lower values for $0.25 < x < 0.75$ composition.

In conclusion, we report the synthesis of 3 nm amorphous Fe–Co–B nanoparticles. Evidence of surface effects at room temperature is observed in the saturation magnetization, remanence and coercive field as a function of Fe/Co ratio. We have interpreted this behaviour as a competition between the two direction of the local surface anisotropy that frustrate the ferromagnetic order of the surface spins of the nanoparticles.

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References

- [1] J.L. Dorman, D. Fiorani (Eds.), *Magnetic Properties of Fine Particles*, North-Holland, Amsterdam, 1992.
- [2] G.C. Hadjipanayis, G.A. Prinz (Eds.), *Science and Technology of Nanostructured Materials*, Plenum Press, New York, 1991.
- [3] J.L. Dorman, D. Fiorani, E. Tronc, *Adv. Chem. Phys.* 98 (1997) 283.
- [4] E. De Biasi, C.A. Ramos, R.D. Zysler, H. Romero, *Phys. Rev. B* 65 (2002) 144416.

- [5] E. De Biasi, C.A. Ramos, R.D. Zysler, H. Romero, D. Fiorani, *J. Magn. Magn. Mater.* 266 (2003) 233.
- [6] J.L. Dorman, D. Fiorani, R. Cherkaoui, E. Tronc, F. Lucari, F. D’Orazio, L. Spinu, M. Nogues, H. Kachkachi, J.P. Jolivet, *J. Magn. Magn. Mater.* 203 (1999) 23.
- [7] R.D. Zysler, C.A. Ramos, H. Romero, A. Ortega, *J. Mater. Sci.* 36 (9) (2001) 2291.
- [8] J.P. Chen, et al., *Phys. Rev. B* 51 (1995) 115.
- [9] R. Gómez-Abal, A.M. Llois, *Phys. Rev. B* 65 (2002) 155426.