Cobalt Ferrite CoxFe3-xO4 (0.4 < x < 0.7) with High Coercive Fields (2000 Oe < Hc < 6000 Oe)

G. Pourroy, S. Läkamp, M. Multigner, A. Hernando, J.-L. Dormann, R. Valenzuela-Monjaras

HAL Id: jpa-00254773
https://hal.science/jpa-00254773

Cobalt Ferrite Co$_x$Fe$_{3-x}$O$_4$ (0.4 < x < 0.7) with High Coercive Fields (2000 Oe < H$_c$ < 6000 Oe)

G. Pourroy, S. Läkamp, M. Multigner*, A. Hernando*, J.-L. Dormann** and R. Valenzuela-Monjaras***

Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Inorganiques, 23 rue du Loess, 67037 Strasbourg cedex, France
* Instituto de Magnetismo Aplicado, Laboratorio "Salvador Velayes", Apdo. Correos 155, 28230 Las Rozas Madrid, Spain
** Laboratoire de Magnétisme et d'Optique de l'Université de Versailles, URA D1531 du CNRS, Bâtiment Fermat, 45 avenue des Etats-Unis, 78035 Versailles cedex, France
*** Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de Mexico, Apartado Postal 70-360, 04510 Mexico D.F., Mexico

Abstract. Cobalt - doped magnetites with coercive fields up to 5400 Oe have been obtained by taking off the metallic part of composites made of iron cobalt alloy and spinel oxide. That results in a decrease of saturation magnetization of composites and to an increase of coercive fields. Most of particles are monodomains. The behavior is interpreted by using the Stoner-Wohlfarth model.

1. INTRODUCTION

Possibilities of obtaining ferrites of spinel structure from metal - ferrite composites have been recently pointed out [1-2]. The ferrites are cobalt doped magnetites which coercive fields can reach high values, 2000 Oe and more [3]. We present here spinel ferrites with different nominal compositions, and study the magnetization process leading to such high coercive field, the origin of the high coercive field and the role that the nanometric soft magnetic Fe - Co inclusions play on the magnetic properties.

2. EXPERIMENTAL

Composites made of iron - cobalt alloy and cobalt doped magnetite have been synthesized by precipitation from Fe(II) and Co(II) chloride solution into 11N boiling KOH [1-2]. The alloy was then chemically eliminated in order to obtain a pure spinel phase. Composite samples labeled 1, 3, 5 and 7 lead to ferrite-only samples 2, 4, 6 and 8.

3. RESULTS AND DISCUSSION

All the samples exhibit well defined XRD patterns with very low background. In samples 1, 3, 5 and 7, a spinel phase and a metallic phase of b.c.c. structure isomorphous of α-Fe occur while the metal has disappeared in samples 2, 4, 6 and 8, i. e. is not visible by XRD and Mössbauer spectroscopy.

Table I - Global composition of the samples, weight increase Δm/m observed by TG in air and the deduced chemical formula, particle sizes observed by SEM, saturation magnetization and coercive field under a 5.5 T magnetic field at room temperature(samples 2, 4, 6 and 8 are obtained by chemical washing of samples 1, 3, 5 and 7).

Samples	global [Co]/[Fe]	Δm/m	Formula	mean size (μm)	Std. Dev (μm)	Median (μm)	M$_s$ (Am^2/kg)	Hc (10^{4}A/m)
1	0.51	6.0%	(Fe$_{0.20}$Co$_{0.80}$)$_{0.44}$(Fe$_{2.38}$Co$_{0.62}$O$_4$)$_{0.51}$				117	12
2	0.27		Fe$_{2.38}$Co$_{0.62}$O$_4$				85	23
3	0.65	6.4%	(Fe$_{0.25}$Co$_{0.75}$)$_{0.49}$(Fe$_{2.16}$Co$_{0.84}$O$_4$)$_{0.51}$	0.76	0.15	0.74	106	20
4	0.38		Fe$_{2.16}$Co$_{0.84}$O$_4$	0.74	0.21	0.68	79	42.5
5	0.66	5.8%	(Fe$_{0.25}$Co$_{0.75}$)$_{0.46}$(Fe$_{2.11}$Co$_{0.89}$O$_4$)$_{0.54}$	0.62	0.11	0.60	95	18.5
6	0.37		Fe$_{2.19}$Co$_{0.81}$O$_4$				81	43
7	0.71	6.4%	(Fe$_{0.25}$Co$_{0.75}$)$_{0.44}$(Fe$_{2.02}$Co$_{0.98}$O$_4$)$_{0.56}$	1.23	0.40	1.23	109	13
8	0.40		Fe$_{2.12}$Co$_{0.88}$O$_4$	1.10	0.22	1.13	91.5	28

The lattice constant of the spinel phase is always equal to 8.399 (1) Å and the unit cell of the b.c.c. phase is equal to 2.838(1) Å for sample 1 corresponding to the composition $Co_{0.8}Fe_{0.2}$ and to 2.840(1) Å for the other samples corresponding to the composition $Co_{0.75}Fe_{0.25}$ [4].TG curves of samples 1, 3, 5 and 7 exhibit a weight increase $\Delta m/m$ above 200°C (Table I), while no variation is observed in vacuum. The chemical formula are deduced from this weight increase and from the composition of the metal (Table I). By chemical washing, the metallic part is eliminated. However, [Co]/[Fe] global ratios of the remaining spinel is lower than in the spinel phase of the composite for samples 5 and 7 because the chemical washing eliminates also the amorphous phases[5]. Scanning electron microscope examinations of the precipitate exhibit octahedral particles which particle sizes are in the submicron range (Table I). Coercive fields and saturation magnetizations are deduced from hysteresis curves measured with a 5.5 T magnetic field. When removing the metal, saturation magnetizations strongly decrease and coercive fields increase. (Fig. 1 and Table I).

In order to give an interpretation of such Hc values, two points have been investigated: a) the particle size distribution and b) the interpretation of the magnetic behavior of the ferrites in the Stoner-Wohlfarth model [6]:

a) The critical particle size separating the single domain structure from the multidomain magnetic structure is usually calculated on the basis of magnetostatic and domain wall energy contributions, leading to a relation of the form $\rho = G\gamma/Ms^2$ where G is a geometrical factor (depending on the particle shape and its corresponding demagnetization factor) and γ is the domain wall energy[7]. For spinel ferrites, calculations result in a critical size value about 0.5 µm. As observed particle sizes are within this range (Table I), at least a high fraction of the ferrite particles should be single domain.

b) Some of the basic assumptions in the Stoner - Wohlfarth model are that uniaxial anisotropy particles are single - domain, noninteracting and randomly distributed in orientation. In such a system, the hysteresis loops have a characteristic shape, tending to a reduced remanence, Mr/Ms near 0.5. This behavior is observed in the ferrite-only samples. Thus, the anisotropy fields can be estimated from the experimental hysteresis loops (Fig.2). They are in good agreement with K values for $Co_xFe_{3-x}O_4$ system obtained by other methods [8]. The small difference in the absolute values can be due to small defects created by the elimination of metal inclusions and to the distribution in particle size. It should be remarked that we consider the particles to be uniaxial just in order to obtain an underestimation of the anisotropy strength.
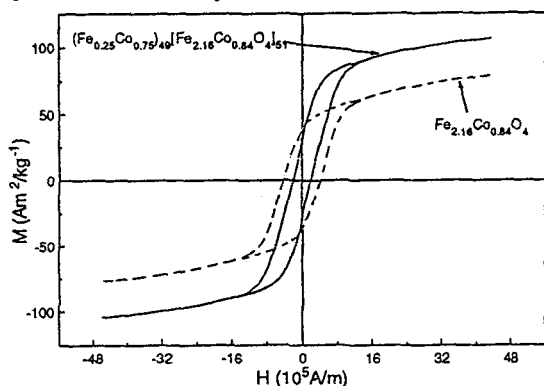

Figure 1: Hysteresis loops of $(Fe_{0.25}Co_{0.75})_{49}(Fe_{2.16}Co_{0.84}O_4)_{51}$ (—) and its corresponding ferrite-only $Fe_{2.16}Co_{0.84}O_4$ (- - -) at room temperature
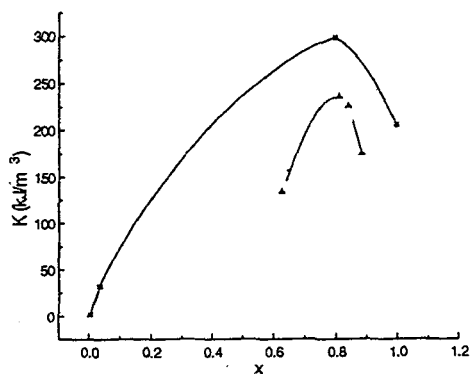
Figure 2: Anisotropy constant for different $Co_xFe_{3-x}O_4$ ferrites versus Co content; reported in ref [8] (■) and calculated for this work(▲)

However, the magnetization does not saturate at high field, in disagreement with Stoner - Wolhfarth model. This could be due to canted spin structure due to the Co substitution and the defects, as observed in similar systems [9]. In addition, the existence of polydomain particles leads to an underestimation of the coercive field of the monodomain particles, therefore an underestimation of the saturating field.

References

[1] Malats i Riera A., Pourroy G. and Poix P. J. Solid State Chem. 108 (1994) 362

[2] Läkamp S., Malats i Riera A., Pourroy G., Poix P., Dormann J.L. and Greneche J. M., Eur. J. Solid State Inorg. Chem. 32 (1995) 159

[3] Malats i Riera A., Pourroy G. andPoix P. J. Magn. Magn. Mat. 134 (1994) 195-8

[4] Pearson W. B., ''Handbook of Lattice Spacings and Structures of metals '' (Pergamon Oxford 1964) p. 505.

[5] Yamegni-Noubeyo J.C., Pourroy G., Werckmann J., Malats i Riera A., Ehret G. and Poix P. J. Am. Ceram. Soc. to be published

[6] Stoner E.C. and Wohlfarth E. P., Phil. Trans. Roy. Soc. A-240 (1948) 599

[7] Valenzuela R. Magnetic Ceramics (Cambridge University Press, Cambridge, 1994) p. 147

[8] Chikazumi C. Physics of Magnetism (Krieger Publishing Company Malabar Florida 1992)

[9] Dormann J. L., Malats i Riera A., Pourroy G. Poix P., Jove J., Renaudin P. Hyperf. Inter. 94 (1994) 1995-8