New Syntheses of Cobalt Ferrite Particles in the Range 2−5 nm: Comparison of the Magnetic Properties of the Nanosized Particles in Dispersed Fluid or in Powder Form

N. Moumen[†] and M. P. Pileni*[,†,‡]

Laboratoire SRSI, URA CNRS 1662, Universite P. et M. Curie (Paris VI), BP 52,
4 Place Jussieu, 75231 Paris Cedex 05, France, and C.E.A.-CE Saclay, DRECAM-S.C.M,
91191 Gif sur Yvette, Cedex, France

Received November 27, 1995. Revised Manuscript Received February 1, 1996[⊗]

The size of cobalt ferrite particles from 2 to 5 nm is controlled by the reactant concentration in oil-in-water micelles. It is possible to obtain the particles either suspended in the solvent to form ferrofluid or in dry powder. When particles are isolated in a fluid, the interactions between particles are small. The magnetic size is similar to that determined by TEM. The reduced susceptibility increases progressively with the size of the particles and does not reach a plateau. With dry powder made of nanosized particles, the magnetic size is higher than that observed by TEM. Likewise, the reduced susceptibility strongly increases with increasing the particle size to reach a plateau for an average size equal to 3 nm. These are explained by the increase in the attractive interactions between particles. By heating the powder, the reduced remanence, M_r/M_s, and the coercivity, H_c, increase with the increase in annealing temperature. This is attributed to the increase in the particle size and to the release of the adsorbed surfactant on the particles. The largest size of particles can be obtained either by annealing of the smallest one or from direct synthesis at room temperature. For a given size, the improvement in coercivity with annealing temperature is attributed to a better-defined nanocrystalline structure and to the release of surfactant to the particle interface.

I. Introduction

Synthesis of nanoparticles, characterized by a low size distribution, is a new challenge in solid-state chemistry. Due to their small size, the nanoparticles exhibit novel material properties which largely differ from the bulk solid state.[1] Many reports[2] on quantum size effect on semiconductor[3,4] or the emergence of metallic properties with the particle size[5−7] have been published during the past few years. A better understanding of magnetism is crucial not only for basic physics but also because of the great technological importance of ferromagnets in information storage,[8] color imaging,[9] bioprocessing,[10] and ferrofluids.[11] Ferromagnetism occurs even for clusters with less than about 30 atoms. As the size increases up to 700 atoms, the magnetic moments approach the bulk limit.[12]

Many investigations have been performed on particle having a size in the range 10−30 nm. A superparamagnetic behavior[13,14] has been found. Small magnetic particles have surface properties that differ from those at the interior. The elucidation of these differences is particularly difficult. The surface morphology depends on the preparation technique and may vary. Passivation[15] and other requirements may introduce more than one phase. The interface and the surface,[16] whether vacuum, gas, or a coating,[17] may change the intrinsic surface properties. Interparticle interactions,[18] especially magnetic ones, may be important. The coating may change the intrinsic surface properties.[13,14]

Magnetic particles, Fe_3O_4, have been obtained on a bilayer lipid membrane. Small particles with magnetic monodomains have been obtained.[19]

Relatively little work exists on magnetic materials having sizes smaller than 10 nm. Nanocrystallites of γ-Fe_2O_3 having an average size of 8 nm have been synthesized by using a polymer matrix.[20] Recently it has been demonstrated that ultrafine cobalt ferrite

---

[*] All correspondence to this author.

[†] Universite P. et M. Curie.

[‡] C.E.A.-CE Saclay.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

(1) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.

(2) Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 6961.

(3) Pileni, M. P.; Motte, L.; Petit, C. *Chem. Mater.* **1992**, *4*, 338.

(4) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477 and reference therein.

(5) Petit, C.; Lixon, M. P.; Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 12974.

(6) Lisiecki, I.; Pileni, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 3887.

(7) Lisiecki, I.; Pileni, M. P. *J. Phys. Chem.* **1995**, *99*, 5077.

(8) Gunther, L. *Phys. World* **1990**, *3*, 28.

(9) Ziolo, R. F. U.S. Patent, 1984.

(10) McMickael, R. D.; Shull, R. D.; Swartzendruber, L. J.; Bennett, L. H.; Watson, R. E. *J. Magn. Magn. Mater.* **1992**, *111*, 29.

(11) Anton, I.; et al. *J. Magn. Magn. Mater.* **1990**, *85*, 219.

(12) Billas, M. L. I.; Châtelain, A.; de Heer, W. A. *Science* **1994**, *265*, 1682.

(13) Haneda, K. *Can. J. Phys.* **1987**, *65*, 1233.

(14) Norrish, A. H. In *Studies of Magnetic Properties of Fine Particles and Their Relevance to Materials Science.* Dormann, J. L., Fiorani, D., Eds.; 1992 Elsevier Science Publishers: Amsterdam, 1992; p 181.

(15) Gangopadhyay, S.; Hadjipanayis, G. C.; Sorensen, C. M.; Klabunde, K. J. *IEEE Trans. Mag.* **1993**, *29*, 2619.

(16) Shinjo, T. *J. Phys.* **1979**, *3*, 6.

(17) Berkowitz, A. E.; Lahut, J. A.; Jacobs, I. S.; Levinson, M.; Forester, D. W. *Phys. Rev. Lett.* **1975**, *34*, 594.

(18) Ferre, R.; Barbara, B.; Fruchart, D.; Wolfers, P. *J. Magn. Magn. Mater.* **1995**, *140*, 385.

(19) Zhao, X. K.; Herve, P. J.; Fendler, J. H. *J. Phys. Chem.* **1989**, *93*, 908.

S0897-4756(95)00556-4 CCC: $12.00

particles used in magnetic fluids are characterized by multiaxial anisotropy.[21] Reverse micelles have been used to synthesize metallic or boride cobalt nanoparticles having an average size equal to 3 and 4 nm, respectively.[22−24]

In the present paper, the magnetic properties of cobalt ferrite, $CoFe_2O_4$, having sizes equal to 2, 3, and 5 nm are compared. These particles are dispersed in a ferrofluid or are in a powder form. The magnetic behavior of particles differs in fluid and in powder with the appearance of superparamagnetic or ferromagnetic regimes. The annealing of the particles in the presence of oxygen induces an increase in the size. This is correlated to the increase in the reduced remanance and coercivity with the increase in the particle size.

II. Experimental Section

II.1. Materials. Sodium dodecyl sulfate (SDS) was bought from BDH, while iron chloride $FeCl_2$ and cobalt acetate, $Co(CH_3CO_2)_2$, were procured from Fluka. Aqueous methylamine, CH_3NH_3OH, was purchased by Merck. All the compounds have been sold as 99.99% purity.

Cobalt(II) and iron(II) dodecyl sulfate, $Co(DS)_2$ and $Fe(DS)_2$, were made as described elsewhere.[25]

II.2. Equipment. Microanalyses (EDS) are obtained with a LINK AN10000 apparatus coupled with a JEOL (JEM100CX2 side entry) electron microscope. A drop of particles dispersed in aqueous solution is evaporated on carbon grid, and the electron micrographs are obtained with a JEOL (Jem 100CX2 top entry) electron microscope.

The ^{57}Fe Mössbauer absorption spectra were recorded using a ^{57}Co*:Rh γ-ray source mounted on a triangular velocity electromagnetic drive. To minimize interaction effects between particles, they were diluted in gelatine; the volume of the sample is 1.57 cm^3, yielding an average distance of response of 30 nm. The experiment was performed at 4.2 K.

To characterize the crystal structure of particles, X-ray diffraction measurements were carried out by using a Stoe Stadi P goniometer with a Siemens Kristaloflex X-ray generator using cobalt cathode driven by a personal computer through the Daco-PM interface.

Small-angle X-ray scattering experiments, SAXS, were performed at the Laboratoire d'Utilisation des Rayonnements Electromagnétiques (L.U.R.E.), C.N.R.S.-C.E.A.-Paris XI, Orsay, France, on the D22 line.

Magnetic studies were performed by using two different equipments. The magnetic curve of $CoFe_2O_4$ powder, at room temperature, has been determined by using a commercial alternative gradient magnetometer (Princeton Measurements Corp. Micromag Model 2900) in a field up to 20 kOe.

The behavior of the particles dispersed in a fluid is studied by using an SQUID magnetometer. To prevent agglomeration, magnetic particles are dispersed in 50% of ethylene glycol in water. The weight fraction of magnetic particles is kept constant and equal to 1%.

III. Size Determination

III.1. By Transmission Electron Microscopy. A drop of the magnetic fluid is placed on a carbon film supported by a copper grid, and the solvent is evaporated.

Histograms are obtained by measuring the diameter, D_i, for an average number of particles close to 500. The standard deviation, σ, is calculated from the following equation:

$$\sigma = \{\sum[n_i(D_i - D)^2]/[N - 1]\}^{1/2}$$

where D and N are the average diameter and the number of particles, respectively.

III.2. By X-ray Diffraction. The X-ray diffractograph exhibits classical line broading associated with a fine particle system. For broad lines, the Debye−Scherrer expression is used to deduce the crystalline size.

III.3. From Small-Angle X-ray Scattering. The scattered intensity $I(q)$ is

$$I(q) = P(q)\ S(q)$$

where q, $P(q)$, and $S(q)$ are the wave vector $4\pi(\sin\theta)/\lambda$ (2θ is the diffusion angle), the form factor, and the structure factor, respectively.

From the form factor, the shape of the aggregates is deduced, whereas the structure factor takes into account interactions between the particles.

To reduce the interactions between particles and to keep the particle stable, the magnetic fluid is diluted with 50% ethyl glycol keeping a weight fraction equal to 0.1%. Hence, the structure factor is assumed to be equal to 1.

The scatter due to a mixture of ethyl glycol−water has been extracted from the total scatter.

The form factor is described by the homogeneous sphere model:

$$P(q) = [(\rho_s - \rho_{CoFe_2O_4})V_{CoFe_2O_4}B(qr_{CoFe_2O_4})]^2$$

$$B(qr_i) = 3\left\{\frac{\sin q\, r_i - qr_i \cos q\, r_i}{(qr_i)^3}\right\}$$

where $V_{CoFe_2O_4}$ and $r_{CoFe_2O_4}$ are the volume and the radius of the particle. The electronic densities of $CoFe_2O_4$, $\rho_{CoFe_2O_4}$, and the solvent, ρ_s, are 1.5 and 0.33 e$^-$ Å^{-3}, respectively.

From the Porod plot ($I(q)\ q^4$ vs q) the characteristic diameter of homogeneous sphere,[26] D_{SAXS}(nm), is related to the first maximum and minimum of this representation, as the following:

$$D_{SAXS} = 0.54/q_{max} = 0.90/q_{min}$$

IV. Treatment of Magnetic Data

The first magnetization curve of each sample is simulated from the Langevin relationship:[27]

$$M(D) = M_s\{\coth(\mu H/kT) - (kT/\mu H)\}$$

with $\mu = \mu(D) = M_s\pi D^3/6$, where M_s and M_s are the total saturation of the overall particles and of the bulk phase, respectively. In a given field H, $M(D)$ is the magnetization of particles characterized by diameter D.

---

(20) Ziolo, R. F.; Giannelis, E. P.; Weinstein, B. A.; O'Horo, M. P.; Ganguly, B. N.; Mehrotra, V.; Russell, M. W.; Huffman, D. R. *Science* **1992**, *257*, 219.

(21) Davies, K. L.; Wells, S.; Upadhyay, R. V.; Charles, S. W.; O'Grady, K.; El Hilo, M.; Meaz, T.; Morup, S., to be published.

(22) Chen, J. P.; Lee, K. M.; Sorensen, C. M.; Klabunde, K. J.; Hadjipanayis, G. C. *J. Appl. Phys.* **1994**, *75*, 5876.

(23) Chen, J. P.; Sorensen, C. M.; Klabunde, K. J.; Hadjipanayis, G. C. *J. Appl. Phys.* **1994**, *76*, 6316.

(24) Petit, C.; Pileni, M. P. J. Magn. Magn. Mater., in press.

(25) Kallay, N.; Pastuvic, M.; Matijevic, E. *J. Colloid Interface Sci.* **1985**, *106*, 452.

(26) *Small Angle X-ray Scatterings*; Glatter, O., Kratky, O., Eds.; Academic Press: New York, 1992.

(27) Charles, S. W.; Popplewell, J. *Ferromagnetic Materials*; Wohlfarth, Ed.; North Holland Publishing: Amsterdam, 1982; Vol. 2.

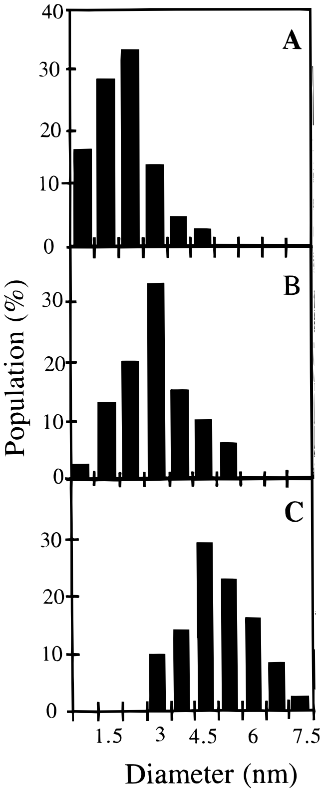

Figure 1. Histograms obtained from TEM patterns of magnetic fluid made at various surfactant concentrations keeping $[Co(DS)_2]/[Fe(DS)_2] = 0.325$, $[Co(DS)_2]/[NH_2CH_3] = 1.3 \times 10^{-2}$. $[Fe(DS)_2] = 6.5 \times 10^{-3}$ M (**A**), $[Fe(DS)_2] = 1.3 \times 10^{-2}$ M (**B**), $[Fe(DS)_2] = 2.6 \times 10^{-2}$ M (**C**).

Assuming a log-normal size distribution, the magnetization of particles at a given field, H, is[27]

$$M = \int M(D)\, P(D)\, \mathrm{d}D$$

where $P(D)$ is the number of particles characterized by a given size, D.

V. Synthesis and Characterization of $CoFe_2O_4$ Nanosized Particles

Recently, syntheses of cobalt ferrite particles differing by their average sizes from 2 to 5 nm have been described:[28] Aqueous methylamine, CH_3NH_3OH, is added to a mixed micellar solution formed by $Co(DS)_2$ and $Fe(DS)_2$ surfactants. The solution is stirred for 2 h at room temperature, and a magnetic precipitate appears. The supernatant is removed and replaced by pure bulk aqueous phase. The precipitate redispersed, and a brown magnetic suspension is obtained. It is usually called magnetic fluid.

The percentage of surfactant remaining in solution is less than 0.1% in weight. The composition in metal of cobalt ferrite particles consists of Fe(III) and Co(II). The syntheses have been performed in an excess of iron(II) because the oxidation yield of Fe(II) in Fe(III) is close to 65%.

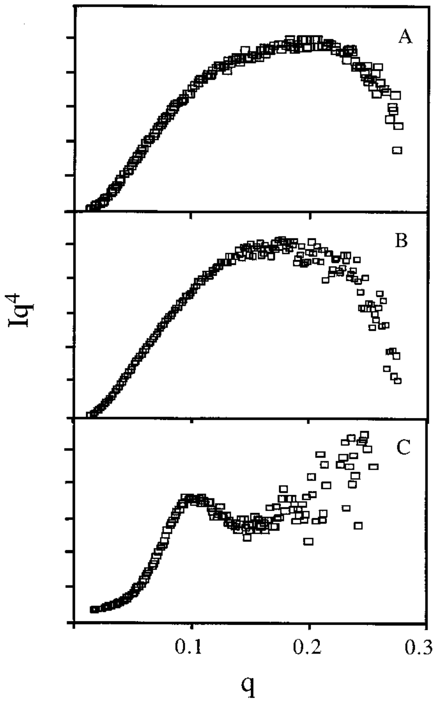

Figure 2. Porod plot, $I(q)q^4$ versus q obtained from SAXS for samples given in Figure 1.

Table 1. Average Diameter of the Particles Deduced from TEM, D_{TEM} (nm), from SAXS, D_{SAXS} (nm), and from Simulation in Magnetic Fluid, D_{MF} (nm), and with Dry Powder, D_{MD} (nm)[a]

D_{TEM} (nm)	2	3	5
D_{SAXS} (nm)	2.6	3.6	5.4
D_{MF} (nm)	2	3	4.2
D_{MD} (nm)	3	3.8	
σ_{TEM} (%)	37	36	23
σ_{M} (%)	42	40	35
σ_{MD} (%)	41	39	
$10^4\chi_{MF}$ (Oe^{-1})	2	3	4
$10^4\chi_{MD}$ (Oe^{-1})	1.75	2.68	2.73

[a] The polydispersity in size determined by TEM, σ_{TEM}, and from simulation, σ_{MF} and σ_{MD}, the susceptibility in magnetic fluid at 200 K, χ_{MF}, and in dry particles at room temperature, χ_{MD}.

Several syntheses have been performed by increasing the $Fe(DS)_2$ concentration, from 6.5×10^{-3} to 2.6×10^{-2} M, keeping the $[Co(DS)_2]/[Fe(DS)_2]$ and $[Fe(DS)_2]/[CH_3NH_3OH]$ ratios equal to 0.325 and 1.3×10^{-2}, respectively. A drop of the magnetic fluid is placed on a carbon film supported by a copper grid. From electron microscopy patterns and histograms, Figure 1 shows an increase in the particle size with the increase in $Fe(DS)_2$ concentration.

By SAXS the average radius of the particles is deduced from a Porod plot. Figure 2 shows a shift to the low q values of the maximum with the increase in $Fe(DS)_2$ concentration. This indicates an increase in the particle size with an increase in $Fe(DS)_2$ concentration. Table 1 shows a good agreement between the size of particles determined from TEM and SAXS.

Electron diffractogram patterns show a good agreement with the intense peaks listed for cobalt ferrite in standard reference tables (Figure 3). This indicates that the particles formed by using a micellar solution have an invert spinel crystalline structure as in the bulk phase.

EDS confirms the relative ratio of cobalt and iron elements in the cobalt ferrite particles (the percentage of the iron and cobalt elements are found equal to 65.63% and 34.37%, respectively).

The Mössbauer spectrum of particles having a 5 nm diameter recorded at 4.2 K (Figure 4) is similar to that

---

(28) Moumen, N.; Pileni, M. P. *J. Magn. Magn. Mater.*, in press.

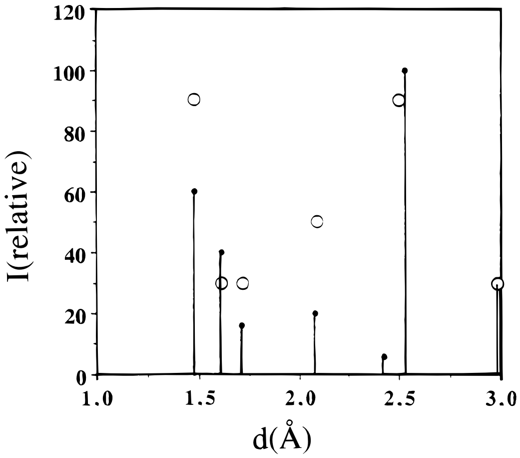

Figure 3. Electron diffractogram of magnetic fluid. The lignes are given by standard reference tables and the point are the experimental data.

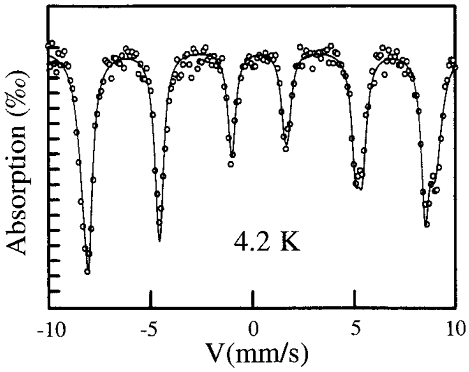

Figure 4. Mossbauer spectrum at 4.2 K of 5 nm diameter particles.

observed for larger particles (30−350 nm) by Haneda and Morrish[29] with the sixth B-site line apparently less intense than the sixth A-site line as is observed for bulk cobalt ferrite. A good fit of the two overlapping six-line hyperfine patterns corresponding to the ^{57}Fe in B and A sites can be obtained with a ratio of A to B site patterns equal to 0.67.

These results are confirmed by X-ray diffraction spectra. A fit of the experimental data yields a value of lattice consistent with bulk cobalt ferrite (8.395).[30] The diffractograph is fitted to a single-phase structure.

VI. Comparison of the Magnetic Behavior of Nanosized Particles Dispersed in an Aqueous Fluid and in Powder Form

From the syntheses described above, particles exist either in a powder form or dispersed in a fluid. It has been chosen to compare the magnetic properties of particles having an average size equal to 2, 3, and 5 nm, respectively.

VI.1. Magnetization. The properties of magnetic fluids made of particles 2, 3, and 5 nm are performed at 200 K. The variation of magnetization, with an applied field, H (kOe), shows no hysteresis; that is, both the remanance and coercivity are zero (Figure 5A,C,E). This indicates a superparamagnetic behavior as expected for nanoscale dimension of the particles. At 300 K, particles having 5 nm as average diameter show a superparamagnetic behavior (Figure 6).

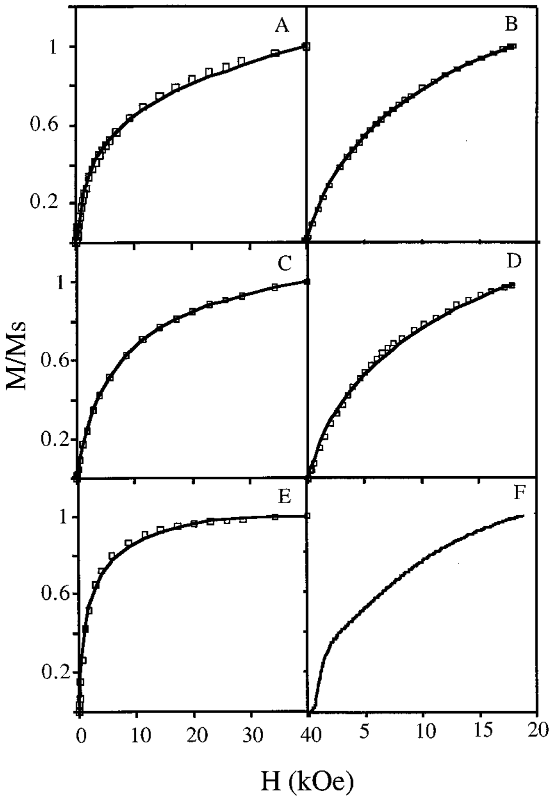

Figure 5. Magnetization as function of applied field at 200 K for particles suspended in a solvent (**A**, **C**, **E**) and at room temperature of dry particles (**B**, **D**, **F**). The size of the particle is 2 nm (**A** and **B**), 3 nm (**C** and **D**), 5 nm (**E** and **F**). (—) experimental data, (□) simulation of langevin law.

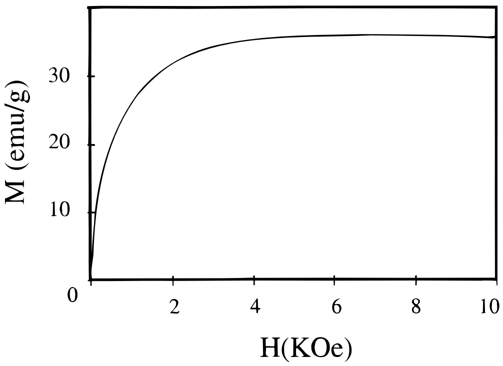

Figure 6. Magnetization as function of applied field at 300 K of 5 nm particles suspended in a solvent.

For dry powder particles, because of experimental limitations, the magnetization curves have been performed at 300 K (Figure 5B,D,F). The appearance of hysteresis with an increase in particle size is observed (Table 2). For particles having an average diameter equal to 2 and 3 nm, the reduced remanance and coercivity are very low. Hence, in a first approximation, a superparamagnetic behavior is assumed for the first magnetization curve. Larger particles behave as a ferromagnet with a too-large hysteresis to assume a superparamagnetic behavior (Table 2).

Hence, at 300 K, particles having an average diameter equal to 5 nm behave as ferromagnets in powder form (Figure 5F) and are in a superparamagnetic regime when they are dispersed in a fluid (Figure 6).

---

(29) Haneda, K.; Morish, A. H. *J. Appl. Phys.* **1988**, *63*, 4258.

(30) Bate, G. *Ferromagnetic Materials*; Wohlfarth, Ed.; 1980; Vol 2, p 431.

Table 2. Variation of the Diameter of the Particle by TEM, D_{TEM} (nm) and by X-ray Diffraction, D_{XP} (nm) the Coercivity, H_c (Oe), and the Reduced Remanance, M_rM_s, before (25 °C) and after Heating the Particles during 30 min at a Given Temperature

	A				B				C			
T (°C)	D_{TEM}	D_{XP}	H_c	M_r/M_s	D_{TEM}	D_{XP}	H_c	M_r/M_s	D_{TEM}	D_{XP}	H_c	M_r/M_s
25	2	2.3	6	0.001	3	3.2	12	0.002	5	5.4	35	0.071
200	2.8	3.1	20	0.03	4.5	5.4	43	0.048	6	7	115	0.127
400	4.6	5.2	154	0.07	5	6.8	148	0.105	6.5	7.9	132	0.160
600	6.1	7.2	254	0.343	6.3	7.8	439	0.407	11.2	12	715	0.443

As expected, in both cases (magnetic fluid and dry powder), the magnetic field needed to reach the saturation magnetization depends on the size of the particles (Figure 5).

VI.2. Average Size Determined from Langevin Curve. For superparamagnetic particles, the magnetic size can be deduced from simulation of Langevin relationship assuming a log-normal size distribution.[31] A good agreement between the simulated and magnetization curves is obtained for magnetic fluids at 200 K and for dry powder made of 2 and 3 nm particles (Figure 5).

The sizes of particles 2, 3, and 5 nm, dispersed in a ferrofluid frozen at 200 K, are in a good agreement to those deduced from TEM (Table 1).

For dry powder, the magnetic sizes of 2 and 3 nm are larger than that obtained above (Table 1). As expected, the first magnetization curve obtained with 5 nm particles does not allow us to deduce a magnetic size from the Langevin curve simulation.

The differences in magnetic size obtained with ferrofluid and dry powder can be attributed to the appearance of interactions between particles. As a matter of fact, in ferrofluid the weight fraction in particles in low (1%). Then the average distance between particles is rather large and the attractive interactions between particles are small or negligible. With dry powder, the average distance between particles is small and the interactions are large. Such interactions perturb the Langevin curve and induce an apparent magnetic size larger than the real one.

VI.3. Reduced Magnetic Susceptibility. The reduced magnetic susceptibility is obtained by dividing the value of the initial slope of the magnetization by the saturation magnetization.

In ferrofluid, the reduced susceptibility of particles having 5 nm as an average diameter is determined at a fixed weight fraction ($\Phi = 1\%$) and two temperatures. It is found equal to 4×10^{-4} Oe^{-1} and 2.6×10^{-4} Oe^{-1} at 200 and 300 K, respectively. For isolated particles, the increase in temperature induces a decrease in the reduced susceptibility. This is due to the increase in the saturation magnetization with decreasing temperature and to the fact that, at low magnetic field, the thermal fluctuations of the material are more sensitive.

At 200 K, the reduced susceptibility increases with the particle size (Figure 7A). These data are consistent with those predicted and observed by Chantrell et al.[31-33] for larger magnetic particles.

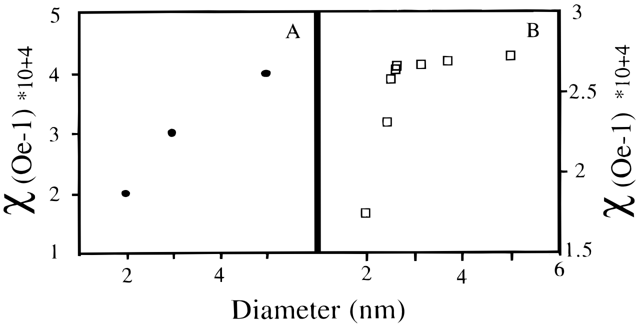

Figure 7. Variation of the reduced susceptibility with the particle sizes obtained at 200 K with diluted particles suspended in a solvent (**A**) and with dry particles at room temperature (**B**).

With dry powder particles, the variation of reduced susceptibility differs with the size range (Figure 7B). Below 3 nm, an increase in the reduced susceptibility with size is observed. Above 3 nm, a plateau is reached. Such behavior is explained in term of interactions. Particles having 2 nm as an average diameter behave as a superparamagnetic system which implies low attractive interactions between particles. This is consistent with a very low remanance and coercivity (Table 2). However these values are not zero indicating some interactions between particles. This is confirmed by the fact that the magnetic size is larger (Table 2) than that determined by T.E.M.

By increasing the particle size, the magnetic interactions increase so much that they lead to a reduction in the change of reduced susceptibility with the increase in the particle size. This is consistent with the appearance of larger hysteresis (Figure 5) and with the increase in the particle size (Table 1).

VII. Influence of Annealing on the Particle Size and in the Magnetic Properties

The particles synthesized and characterized above are heated for 30 min at 200, 400, and 600 K in the presence of air. Because of the increase in the average size with increasing temperature, the particles obtained at room temperature having an average diameter equal to 2, 3, and 5 nm are called particles **A**, **B**, and **C**, respectively.

For the various samples, EDS shows no changes in the composition compared to that obtained at room temperature (Fe 65.63%; Co 34.37%). From X-ray diffraction, it is impossible to know if the cation site distribution changes with the increase in temperature. The weight of the sample decreases when the particles are heated. This is attributed to the leaving of water molecules from the crystal and of the surfactant molecules adsorbed at the particle interface.

For particles **A**, X-ray diffractogram spectra (Figure 8) show a broad peak at 25 °C which get increasingly narrow by increasing the temperature to 600 °C. The

---

(31) Chantrell, R. W.; Popplewell, J.; Charles, S. W. *Physica* **1977**, *86–88B*, 1421.

(32) Chantrell, R. W.; Popplewell, J.; Charles, S. W. *IEEE Trans. Magn.* **1978**, *14*, 975.

(33) Chantrell, R. W.; Bradbury, A.; Popplewell, J.; Charles, S. W. *J. Appl. Phys.* **1982**, *53*, 2742.

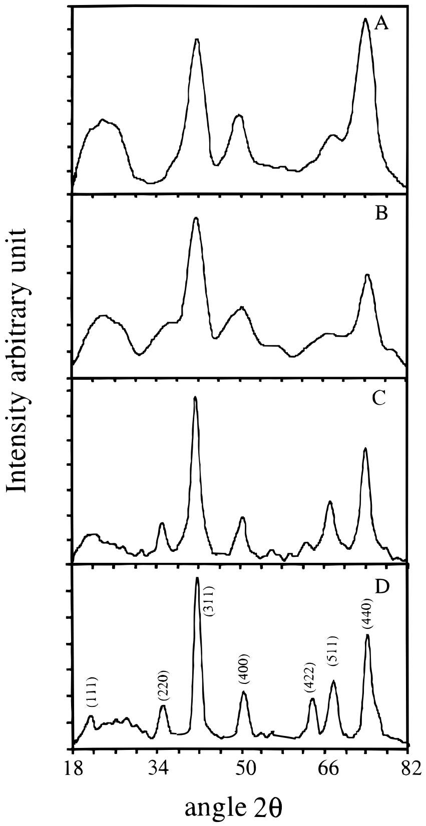

Figure 8. X-ray diffractogram of 2 nm particles heated at various temperatures for 2 h: (**A**) 25, (**B**) 200, (**C**) 400, and (**D**) 600 °C.

decrease in the width of the peaks is attributed to an increase in the particle size. This is confirmed by the TEM pattern and histograms given in Figure 9. Hence, an increase in the size distribution with the increase in annealing temperature is observed. A good agreement between the size of the particles determined from X-rays diffractograph and from TEM is obtained. However the size determined from the Debye–Scherrer expression is always larger than those by TEM (Table 2). These differences are due to the mode in the size determination: by X-ray diffraction and TEM, it is assumed to be a volume and a radius distribution, respectively.

Similar behavior as described for **A** particles has been observed for **B** and **C**. An increase in the particle size is observed with the increase in temperature. From 25 and 600 °C the particles remain spherical. Table 2 summarizes the data deduced from X-ray diffraction spectra, TEM.

Magnetization studies were performed, at room temperature, on powders by using a commercial alternative gradient magnetometer. The reduced remanence, M_r/M_s, and the coercivity, H_c, increase with the increase in annealing temperature. Figure 9 and Table 2 shows an increase in the size of the particle with increasing the annealing temperature. However, the annealed particles remain in the single domain range. Hence the increase of M_r/M_s and H_c can be attributed to (i) the increase in the particle size and (ii) the release of the adsorbed surfactant on the particles. As matter of fact, it has been well demonstrated[13,34,35] that compounds absorbed on the interface induces a decrease in saturation magnetization and in coercivity. In our experimental conditions the release of the surfactant is observed by the decrease in the weight of the particles after heating.

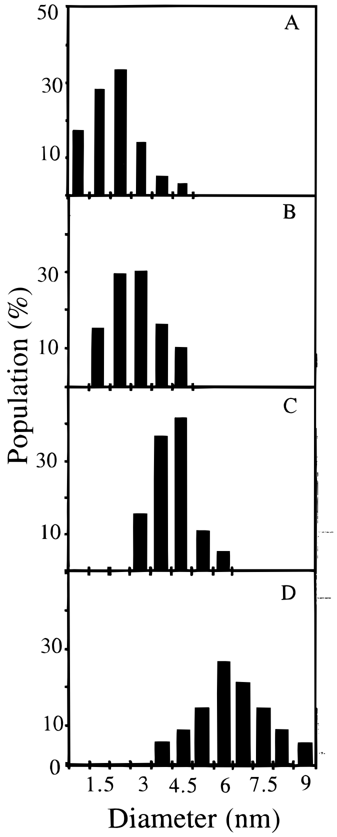

Figure 9. Histograms from TEM patterns obtained for 2 nm particles heated at various temperatures for 2 h: (**A**) 25, (**B**) 200, (**C**) 400, and (**D**) 600 °C.

The largest size of particles can be obtained either by annealing the smallest one or from direct synthesis as described above.

The heat of 2 nm particles to 400 K induces an increase in the average size of the particles to 4.6 nm with a coercivity equal to 154 Oe, whereas 5 nm particles made at room temperature are characterized by a coercivity equal to 35 Oe. Similar behaviors are shown in Table 2. Hence, for a given size, the coercivity increases with annealing temperature. This improvement in coercivity is associated with (i) a better defined nanocrystalline structure due to anneal and (ii) the release of surfactant to the particle interface.

VIII. Conclusion

In this paper the magnetic behavior of particles differing by their size and in various media has been compared. The particles having 2, 3, and 5 nm are either dispersed in a fluid to form a so-called ferrofluid or in a dry powder.

In ferrofluid, the interactions between particles are small. Hence the magnetic size is similar to that determined by TEM. Likewise, the reduced susceptibility increases progressively with the particle size and does not reach a plateau.

For a dry powder made of nanosized particles, the magnetic behavior strongly differs. For small particles

---

(34) Berkowitz, A. E.; Lahut, J. A.; VanBuren, C. E. *IEEE Trans. Magn.* **1980**, *16*, 184.

(35) Haneda, K.; Morrish, A. H. *IEEE Trans. Mag.* **1989**, *25*, 2597.

(2 and 3 nm diameter), in a first approximation, can be assumed a superparamagnetic behavior. However, the magnetic size is larger than that determined by TEM. Likewise, the reduced susceptibility increases drastically from 2 to 3 nm and then reaches a plateau. These data are explained in term of an increase in the attractive interactions between particles.

By heating the powder made of nanosized particles, the reduced remanance, M_r/M_s, and the coercivity, H_c, increase with the increase in annealing temperature. This is attributed to the increase in the particle size and to the release of the adsorbed surfactant on the particles. The largest size of particles can be obtained either by annealing of the smallest one or from direct synthesis at room temperature. For a given size, the improvement in coercivity with annealing temperature is attributed to a better defined nanocrystalline structure and to the release of surfactant to the particle interface.

Acknowledgment. The authors would like to thank Dr. P. Veillet for fruitful discussions and Dr. P. Bonville for allowing us to publish the Mossbauer spectrum of cobalt ferrite having an average size equal to 5 nm.

CM950556Z