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Synthesis and structural characterization of Co immersed in Ag nanoparticles obtained by successive reactions in microemulsions

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Abstract

Co@Ag nanoparticles have been prepared in microemulsions by the successive reaction technique. It was observed that, under the experimental conditions of this study, the size of the Co nuclei is limited by the reactant concentration (approx. 0.7 nm), whereas the Ag covering is templated by the microemulsion droplet size (approx. 7 nm). The as-prepared particles mainly contain clusters in the form of Co_3O_4 , which evolves to Co as the samples are annealed in a reducing atmosphere at high temperatures. At temperatures >300 °C the pasivating surfactant layer decomposes with the subsequent growth of the nanoparticles, converging their properties to Co and Ag bulk. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

Magnetic systems based on nanoparticles/clusters are nowadays a very important topic of research because of their potential applications in a great variety of different fields, like magnetic storage, ferrofluids, drug delivery, magnetic paints, magnetic ceramics, magnetic imaging, etc. [1] On the other hand, from the scientific point of view, there are many properties which are not well-known, because these mesoscopic systems may behave differently from both the bulk materials and also the isolated atoms/ molecules. Just as an example, a typical diamagnetic material, like Au, becomes apparently ferromagnetic at room temperature in the presence of a thiol, when the size is reduced down to approx. 1 nm [2]. Because of the importance of the nanomaterials, in the last years new methods for the production of nanoparticles (NPs) and clusters have been developed with the aim of controlling by a simple way the size and shape of the NPs. New developments are expected in this field related to the production of well-defined hybrid or composite

nanomaterials, like those composed of magnetic and nonmagnetic parts. Good examples of this type of materials are magnetic granular solids formed by magnetic NPs immersed in an isolated matrix, like Fe@Au, Fe@Cu, Co@Ag, Co@Cu, etc. The presence of ferro- and antiferromagnetic phases near the particle surfaces (for example, due to the partial oxidation of the surface NPs inside the matrix) can induce dramatic changes in the magnetic properties of the NPs, like those reported recently for Co@CoO by Skumryev et al. [3]. They show that magnetic exchange coupling induced at the interface between Co ferromagnetic nanoparticles and paramagnetic (C or Al₂O₃) or antiferromagnetic (CoO) systems provides an extra source of large effective anisotropy. This leads to a marked improvement in the thermal stability of the magnetic moments of the ferromagnetic nanoparticles.

All the mentioned examples clearly show that the final (electrical, magnetic, etc.) properties are highly dependent on the synthesis conditions. Therefore, the knowledge of the composition, structure, size and shape are the key to understand the new properties which appear in these systems, particularly at the nanometer-subnanometer scale.

In the present work we will show the synthesis and structural characterization of Co clusters immersed in Ag NPs prepared by the microemulsion technique [4]. It will be shown how by performing successive reactions in

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microemulsions [5] it is possible to control the sizes of both, Co clusters and Ag NPs. X-ray diffraction, TEM and EXAFS techniques are used to know the as-prepared samples and to follow the evolution of the structure after heat treatments in different atmospheres.

2. Experimental

2.1. Introduction

The microemulsions employed in the production of the particles were composed of *n*-heptane, aqueous solution, and aerosol-OT (*AOT*, sodium dodecylsulphosuccinate). In the presence of large amounts of heptane water-in-oil (W/O) microemulsions are formed. The size of the water nanodroplets can be controlled [6] by the ratio $R = [H_2O]/$ [AOT], and is given by the following Eq. [7]

$$r(nm) = 1.5 + 0.18R \tag{1}$$

It is worth to mention that in this type of microemulsions, for R < 10, most of the water inside the droplets is not free [8], but it is fixed by the surfactant heads. For R > 10 water becomes more free to move and, as R increases, it becomes to behave like bulk water.

For the synthesis of NPs by the microemulsion technique it is usual to prepare two similar W/O microemulsions carrying the reactants. After mixing both microemulsions a fast material exchange [9] takes place and the reactants can then react in the interior of the nanodroplets. Microemulsion droplets are rather monodisperse; therefore, by controlling the droplet size, it was assumed that particles of different sizes could be obtained. This has been observed to occur in various systems, like, e.g. Fe oxide NPs in AOT microemulsions [10] and ethylenoxide microemulsions [11]. However, in other cases the particle size seems not to depend on the droplet size, as, e.g. Pt NPs prepared in ethylenoxide microemulsions [12]. It is now recognized that microemulsions are not real templates, and that there are other factors, like concentration of reactants, film flexibility, etc. [13], which play an important role in determining the final particle size. In this work, we have taken into account this information to prepare the Co@Ag nanoparticles.

Once the reaction is finished, surfactant is attached to the particle surfaces inhibiting their further growth [8] or promoting the formation of particles of special shapes if there are aged for some time in the microemulsion reaction media [14]. In our case, a short aging of the as-prepared particles was carried out to allow the AOT to be attached to the NPs.

2.2. Synthesis of Co and Ag by chemical reduction of metallic salts by NaBH₄

Reduction of an aqueous solution of metallic salts by an appropriate reductant allows the preparation of metal

particles [15,16] Natrium borohidryde is one of the most used reduction agents for metals [17] which can also give rise to the formation of borides [17]. The final composition depends on different factors, like temperature, reaction media, etc. For the particular case of Co, it has been shown that, in aqueous media, the main products of the reduction with NaBH₄ are boron compounds: Co_2B and $Co(BO_2)_2$. Metallic Co is only present as a minor secondary product of the reaction [15]. On the other hand, in the absence of water, reduction of Co²⁺ by NaBH₄ gives preferentially metallic Co [16]. As we have already mentioned, in microemulsions with low R values (conditions used in this work), water is mainly linked and highly immobilized by the surfactant heads. Therefore, these low R conditions are similar to those used to obtain metallic Co in bulk, and no boron compounds are expected to be formed.

Ag particles are easier to prepare than Co particles so that softer reductants than $NaBH_4$ can be used. However, in order to make the whole process simpler we have used in this work borohydride to produce also Ag shells [18–20], as a matrix around the Co clusters.

2.3. Sample preparation

The ratio *R* was set at different values between R=3 and 10. The whole process for obtaining the particles was carried out in an inert glove box. For the formation of the cobalt cores two different microemulsions were prepared. The first one consisted of an aqueous solution of Co(NO₃)₂×6H₂O (0.1 M) and the second one contained NaBH₄ (0.2 M). The two microemulsions were mixed and the cobalt particles were formed inside the nanodroplets (they are represented by a black dot in the schematic picture shown in the Fig. 1).

In a second step, solid NaBH₄ was added in excess and then an aqueous solution containing $AgNO_3$ with a previously established molar ratio was poured over this microemulsion containing the magnetic cores. The Ag^+ ions can only be reduced within the nanodroplets containing the Co particles. This process prevents surfactant to be present at the Co/Ag interface. After a short aging (approx. 10 min), the nanoparticles were separated from the solution by ultracentrifugation, washed several times with *n*-heptane and ethanol, and finally dried with acetone.

Co/Ag molar ratio was fixed at different values between 1/5 and 1/15. Samples of Co without Ag covering were also prepared for comparison purposes.

The as-obtained particles were subsequent annealed in different atmospheres (H₂, Ar or O₂), at different temperatures in the range $100 \le T_a(^\circ\text{C}) \le 700$.

In Fig. 1 the general scheme of the sample preparation is shown.

For further discussions it is interesting to make an estimation of the local concentration of the reactants inside the microemulsion droplets. For R=3 and 10, according to Eq. (1), droplets with sizes of d=4.1 and 6.6 nm should be



Fig. 1. Schematic representation of the sample preparation.

obtained. This implies droplet volumes of 0.36×10^{-19} cm³ and 1.5×10^{-19} cm³, respectively. From the used cobalt concentration, $[\text{Co}^{2+}]=0.1$ M, one can deduce a concentration of 2 and 9 metallic ions/droplet, respectively.

2.4. Experimental characterization

For the chemical analysis of the samples, the *neutron* activation technique (Centro Atomico de Bariloche, Argentine) and the atomic emission spectroscopy technique (Ar plasma ICP, Perkin Elmer 5500, with Scotten Ryton nebulization chamber and cross flux nebulization) were employed. Very good agreements between both techniques were obtained. Thermogravimetric analysis (TGA, Perkin Elmer) was used to study the evolution of the samples treated at different temperatures.

The local structure of the nanoparticles was studied by *X*-ray absorption spectroscopy (XAS), *X*-ray diffraction (XRD), and transmission electron microscopy (TEM). For TEM analysis two equipments were used to get microphotographs and diffraction patterns: Phillips CM200 and JEOL 2010 both running at 200 kV (λ =0.0251 Å). Samples were prepared dispersing the particles in ethanol depositing one drop onto a carbon-coated Cu grid (sample-screen distance: *L*=1.5 m).



Fig. 2. Weight loss of a typical Co@Ag sample after heat treatment.

For the XRD measurements, a Philips PW-1710 diffractometer with a Cu anode operating at 40 kV was employed. The radiation used corresponds to the $K_{\alpha 1}$ and $K_{\alpha 2}$, transitions, with an average $\lambda = 1.542$ Å. All the XRD measurements were carried out at room temperature.

The EXAFS (extended X-ray absorption fine structure) measurements were performed on the DCI ring of LURE (France), at the Co K-edge on samples made of compacted powder (pressed at 10 Tm), using the total electron yield detection mode at 80 K. The monochromator was equipped with Si [111] crystals. Samples were fixed to the sample holder using a Ag paint. Typically 2-4 scans with 2 eV energy steps on a 1000 eV range after the edge, were recorded on each sample in order to get a good signal to noise ratio. Standards of pure Co and Co₃O₄ were measured in similar conditions. From the raw data (see e.g. Fig. 6) EXAFS oscillations were extracted following standard procedures [21-23] After subtracting the pre-edge, the atomic absorption was removed using a 5 degree polynomial. The obtained $\chi(k)$ spectrum was multiplied by k^3 , then Fourier transformed through a Kaiser window [24] with $\tau = 2.5$, to get a pseudo radial function representative of the atomic distribution around the absorber. The k interval was chosen with extreme values 3 and 10 rad/Å. The following step consists in isolating the first peaks and performing their inverted Fourier transform, obtaining the contribution to the signal which is just due to that shells. This filtered signal is fitted to the equation of the EXAFS oscillations, getting structural parameters, like the number N of atoms in the shell, the distance r from

able 1					
nalysis	of some	representative	samples (in	weight	percentage)

	%Co	%Ag	Rests	Co/Ag
Co	5.77 ± 0.07	0	94.23 ± 0.07	_
Co@Ag	2.48 ± 0.05	41.2 ± 0.8	56.3 ± 0.8	1/9
Co@Ag ^a	2.90 ± 0.06	59.1 ± 0.8	38.0 ± 0.8	1/11

^a Sample treated at $T_a = 300$ °C for 5 h.

т



Fig. 3. Microphotograph and particle size distribution of Co@Ag nanoparticles prepared in microemulsions with R = 10.

the shell to the central atom and a factor of disorder σ . In order to perform the fittings, we used phase and amplitude extracted from the experimental and calculated signals for Co–Co, Co–O [25,26] and Co–Ag [27].

3. Results and discussion

3.1. Analytical characterization

In Fig. 2, the thermal evolution of the mass loss for a Co@Ag sample is shown. The weight loss at about 100 °C is due to the evaporation of water, whereas the losses at around 300 °C are due to the surfactant decomposition. It will be seen later on that the surfactant loss at high temperatures yields to particle aggregation and growth.

In Table 1, the weight percentages of Co and Ag in some typical samples is shown. Co/Ag molar ratios are also shown. They compare well with the used experimental ratios (1/10 for the samples shown in the table).



Fig. 4. XRD and ED of as-prepared and termal treated Co@Ag NPs.



Fig. 5. Micrograph and XRD of a non-coated Co sample.

3.2. Structural characterization

3.2.1. TEM, XRD and ED

3.2.1.1. As-prepared Co@Ag samples. In Fig. 3, a TEM microphotograph of the final Co@Ag nanoparticles is shown. From the corresponding size histogram it can be seen that the final particle size is 7.1 ± 2.3 nm, which agrees very well with the droplet size used for these samples (R = 10, d = 6.6 nm).

Fig. 4 shows a typical XRD pattern and electronic diffraction (ED) of the as-prepared samples. It can be clearly seen the presence of rings and peaks which can be identified with the presence of nanocrystalline Ag [28], although a small bias in the position of the peaks towards high scattering angles ($\Delta \theta \approx 0.1^{\circ}$) is observed. This could be associated with the small size of the particles, but also with possible tensions generated by the presence of immiscible Co clusters in the interior of the Ag particles. From the broadening of the peaks one can estimate the crystalline size using the Scherrer formula [29] ($0.9\lambda/\Gamma \cos \theta$). The size estimated in this way ($\approx 10 \text{ nm}$) agrees with the estimation made from the TEM pictures (Fig. 3).



Fig. 6. EXAFS of an as-prepared Co sample in comparison with the spectra observed for metallic Co and Co_3O_4 .



Fig. 7. Pseudo-radial distribution function of an as-prepared Co sample and standard cobalt oxide.

3.2.1.2. As-prepared non-coated Co particles. Fig. 5 shows a TEM microphotograph of the Co particles prepared without Ag coating. Presence of particles with sizes smaller than 1 nm dispersed in a surfactant matrix is observed. Because of the very small size of the particles the precise estimation of the size is very difficult. The XRD showed in the same figure is characteristic of amorphous or very small particles [30] and, in this sense, agrees with the TEM pictures. Two small peaks can however be resolved, located at approx. 35° and 61° , which could be associated with the presence of Co oxides [28], although a displacement of the peaks towards lower angles is again observed. The presence of such displacements can be associated with an increase of the interatomic distances in these very small systems and is also observed by EXAFS as show below.

3.2.2. EXAFS

3.2.2.1. As-prepared non-coated Co particles. In Fig. 6, the characteristic absorption spectrum of the as-prepared Co particles is shown. In the same figure, the spectra of standard samples of metallic Co and Co_3O_4 , is also shown. The graphics have been displaced in order to get an easier comparison. It can be qualitatively observed that the spectra of the Co samples are more similar to the Co oxide than to the metallic Co.

In Fig. 7 a comparison of the *pseudo-radial distribution function* of the cobalt oxide standard sample and the Co particles is made. As it can be seen the Fourier transform, calculated from the EXAFS oscillations, shows the presence of a peak at a short distance (<2 Å), which can be associated with Co–O. Another peak located at larger distances (2.6 Å) can also be observed. This peak can be associated with a Co–Co neighbour contribution.

3.2.2.2. As-prepared Co@Ag samples. In Fig. 8(a) it can be seen the EXAFS of Co particles covered by Ag. It can be observed that the oxidation of Co is larger than the Co



Fig. 8. (a) Pseudo-radial distribution function of Co and Co@Ag NPs (b) Change of the Co neighbours with the Co/Ag molar ratio for different R values.



Annealed Co@Ag

Fig. 9. Micrographs and particle size distribution of Co@Ag sampes after heat treatment: (a) $T_a = 300$ °C, (b) $T_a = 500$ °C (negative).



Annealed cobalt particles

Fig. 10. Evolution of the XRD patterns with temperature for non-coated Co particles.



Fig. 11. EXAFS and pseudo-radial distribution functions for Co and Co@Ag samples after heat treatments. As-prepared samples and metallic Co is also shown for comparison purposes.

particles without covering. The number of Co neighbours decreases as the Ag coating increases (Fig. 8(b)).

This behaviour can be understood taking into account the difference in the redox potentials of Co and Ag. The redox potential of Co is negative, whereas Ag has a positive redox potential. This means that the Ag coating can easily oxidize the Co particles at the interfacial layer, and this process will be more important as the amount of Ag is increased. It is convenient to mention here that when the covering is made with a less noble metal, like Cu, the oxidation is reduced in comparison with Ag, as it has been shown before [31].

The low number of coordination, *N*, obtained from the fittings is due to the small size of the Co particles/clusters. From the coordination number one can estimate the size of these clusters (d) using the following relationship given by Borowski [32]

$$\frac{N(r)}{N_{\infty}} = 1 - \frac{3r}{2d} + \frac{r^3}{2d^3}$$
(2)

N(r) represents the average number of neighbour atoms located at a distance r from the central Co atom; N_{∞} represents the similar number in bulk. In our case we can deduce that $r \approx 2.5$ Å and $N(r)/N_{\infty} \approx 0.5$. Then, one can obtain for the Co clusters a size of $d \approx 72$ nm, which means $V \approx 2.0 \times 10^{-22}$ cm³/cluster. Assuming a density of 6.1 g/ cm³ for Co oxide, one can estimate a number of 9 Co atoms per cluster. This value agrees very well with the number of Co atoms calculated from magnetic measurements (11 Co atoms/cluster) [33], and also with the TEM pictures (d < 1 nm).

It can be observed that the final Co particle size is not templated by the microemulsion droplet size (6.6 nm), but by the droplet concentration (9 Co ions/droplet). Monte Carlo computer simulations [34] have predict this kind of behaviour when the reactant concentration is small and the reaction is carried out with relatively rigid surfactant films, like the AOT used in the present work. On the contrary, the final size of the Ag nanoparticles, used as coatings, is templated by the microemulsion droplets (see Section 3.2.1.1). Because the size of the imbibed Co clusters is



Fig. 12. Filtered signal of the first peak of the Fourier transform for a Co@Ag sample.

Table 2 Change of the neighbour oxygen and cobalt atoms (around a central Co atom), N, as a function of the annealing temperature (T_a)

$T_{\rm a}(^{\circ}{\rm C})$ (Ar,	No		N _{Co}	N _{Co}	
1 h)	Co@Ag	Co@Cu	Co@Ag	Co@Cu	
As-prepared	3.02	7.00	1.80	0.00	
400	_	3.20	_	0.50	
500	2.98	2.20	2.00	2.50	
600	_	0.00	_	9.50	
700	2.48	_	7.00	-	

Table 3

Change of the neighbour oxygen and cobalt atoms (around a central Co atom), N, as a function of the different annealing atmospheres

		No	N_{Co}
Annealing atm. (500 °C, 1 h.)	As-prepared	3.10	1.75
	O_2	3.00	2.00
	Ar	2.75	2.10
	H_2	0.10	10.0
	Metallic Co	0	12

very small compared to the Ag coating particles ($d_{\text{Co@Ag}}_{\text{particles}} \sim 10 d_{\text{Co cluster}}$), the number of Co clusters immersed in the Ag particles is around 90 Co clusters per Co@Ag particle, for a typical Co/Ag ratio of 10.

3.3. Thermal treatments

The as-prepared samples were subjected to different heat treatments. Fig. 9(a) shows that when the particles are heated to 300 °C, they begin to aggregate. Below this temperature no difference in size is observed. When the temperature is increased to 500 °C the aggregation proceed further and larger particles ($d=23\pm4$ nm) are formed (see Fig. 9(b)). In this case the surfactant decomposition (see Fig. 2) and the Ag melting are the main parameters promoting the growth (it is known that the melting point of metals is largely reduced for metal particles [35]).

Moreover, as expected, heat treatment promotes the particle crystallization and the increase of the crystal domains. In Fig. 4 the evolution of the XRD and ED with the temperature is shown. Samples heated to 200 °C show much more clear crystal diffraction patterns than the as-prepared samples. All the diffraction peaks correspond to the cubic Ag covered matrix. One can clearly observe the decrease of the peak width by increasing the temperature. From this width, one can estimate the crystal domain sizes (≈ 20 nm) which turned out to be similar to those deduced from the TEM pictures. At the same time, heat treatments suppress the bias detected in the peak positions for the as-prepared samples, indicating that the high temperature annealing eliminate the tensions observed in this small composite particles.

In Fig. 10, the evolution of the X-ray diffraction patterns with temperature for a non-coated Co sample under different atmospheres, is shown. Heat treatments (both in Ar and H₂) below 300 °C do not produce appreciable changes. However, for treatments at $T_a \ge 300$ °C, especially in H₂, it is observed the crystallization of cubic metallic Co. In Fig. 11, the evolution of the pseudo-radial distribution function with the heat treatments, is shown. It can be also observed how the thermal annealing transforms the oxidized Co clusters into metallic ones. By performing fittings similar to those shown in Fig. 12, one finally can get the results shown in Tables 2, 3 and Fig. 15.

In Table 2 and Fig. 13, the number of oxygen ($N_{\rm O}$) and cobalt ($N_{\rm Co}$) neighbour atoms obtained from the fittings for different annealing temperatures, $T_{\rm a}$, is shown (results for Co/Cu samples previously obtained [31] are also shown for comparison). It is observed that the amount of Co oxide diminishes as $T_{\rm a}$ increases, giving rise to the formation of metallic Co. This tendency is stronger when a H₂ atmosphere is used (Table 3 and Fig. 14).

It can be also noted that the total number of Co atoms around the central one increases with the annealing temperature indicating the growth of the clusters. By applying Eq. (2) one can deduce that, for a sample treated at 500 °C in H₂, $N(r)/N_{\infty} \approx 0.8 \Rightarrow d \approx 2$ nm, i.e. the Co clusters are approx. 20 times larger (in volume) than in



Fig. 13. Data shown in Table 2.



Fig. 15. Change in the Co–O and Co–Co distances with the annealing temperature.

the as-prepared samples. This increase can be associated with the increase of the phase segregation tendency as the temperature rises. This driving force pushes together the imbibed Co clusters, which now can easily move in the more fluid Ag particle matrix, giving rise to the observed increase in the Co cluster size.

Another interesting point, related with the interatomic (Co–O and Co–Co) distances, can be pointed out. As it can be observed in Fig. 15 these distances decrease as the annealing temperature is increased, converging to the typical bulk distances. This result agrees with what is observed by XRD (see Section 3.2.1).

In some cases, a third distance can be distinguished from the fittings. This distance can be associated with a Co–Ag interaction. The corresponding distance is relatively large (~3 Å), which indicates the relative soft interaction between Co and Ag due to their immiscibility. Fig. 16 is an example of the goodness of the fittings which can be made with the three mentioned different distances and type of neighbours.



Fig. 16. EXAFS oscillations in a Co@Ag sample fitted assuming three superimposed contributions: Co–Co, Co–O and Co–Ag.

4. Conclusions

It has been described a method to prepare clusters of Co imbibed in Ag nanoparticles by performing successive reactions in AOT-based microemulsions. Chemical analysis of the prepared particles shows the presence of Co and Ag in similar ratios to the experimental ones. The Co@Agcomposite nanoparticles are protected from growing by the attached AOT. When the surfactant is decomposed at high temperatures (T > 300 °C) aggregation of both, Co clusters (inside the particles) and Ag coating particles is produced.

TEM pictures show that *Co@Ag* particles are relatively spherical, monodisperse and with sizes similar to the microemulsion droplets. The imbibed Co cluster sizes are controlled, on the contrary, by the small used ion concentration inside the droplets.

An EXAFS characterization of the Co clusters was carried out showing that, the as prepared samples are formed by approx. 10 atoms of Co mainly oxidized in the form of Co_3O_4 . The oxidation increases as the Ag/Co ratio also increases. When the samples are annealed at different temperatures in reducing atmospheres the transition to metallic Co is observed together with the increase in both, the Co cluster and the global Co@Ag particle size.

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References

- A.J. Freeman, C. Li, R.Q. Wu, in: G.C. Hadjipanayis, G.A. Prinz (Eds.), Science and Technology of Nanostructured Magnetic Materials Nato. Adv. Study Inst. Series B vol. 259, Plenum, New York, 1991.
- [2] P. Crespo, R. Litran, T.C. Rojas, M. Multigner, J.M. de la Fuente, J.C. Sanchez Lopez, M.A. Garcia, A. Hernando, S. Penades, A. Fernandez, Phys. Rev. Lett. 93 (2004) 087204.
- [3] V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, J. Nogues, Nature 423 (2003) 850.
- [4] M.A. Lopez Quintela, J. Rivas, J. Colloid Interface Sci. 158 (1993) 446.
- [5] M.A. Lopez-Quintela, Curr. Opin. Colloid Interface Sci. 8 (2003) 137.
- [6] P.D.I. Fletcher, A.M. Howe, B.H. Robinson, J. Chem. Soc. Faraday Trans. I 83 (1987) 985.
- [7] M.P. Pileni, Adv. Colloid Interface Sci. 46 (1993) 139.
- [8] P. Stenius, in: P.L. Luisi, B.E. Shaub (Eds.), Reverse Micelles, Plenum Press, New York, 1984.
- [9] H.F. Eicke, J.C.W. Shepherd, A. Steinmann, J. Colloid Interface Sci. 56 (1976) 168.
- [10] M.A. Lopez-Quintela, J. Quiben, J. Rivas, in: C. Solans, H. Kunieda (Eds.), Industrial Applications of Microemulsions Surfactant Science Series, Marcel Dekker, New York, 1997, pp. 247–265.
- [11] J.A. Lopez Perez, M.A. Lopez-Quintela, J. Rivas, J. Mira, S.W. Charles, J. Phys. Chem. B 101 (1997) 8045.
- [12] J.F. Rivadulla, M.C. Vergara, M.C. Blanco, M.A. Lopez Quintela, J. Rivas, J. Phys. Chem. B 101 (1997) 8997.
- [13] M.A. Lopez-Quintela, J. Rivas, M.C. Blanco, C. Tojo, Synthesis of nanoparticles in microemulsions, in: L.M. Liz Marzán, P.V. Kamat (Eds.), Nanoscale Materials, Kluwer, 2003, pp. 135–155. (Chapter 6).
- [14] D. Kuang, A. Xu, Y. Fang, H. Ou, H. Liu, J. Crystal Growth 244 (2002) 379.
- [15] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Langmuir 8 (1992) 771.
- [16] G.N. Glavee, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Inorg. Chem. 32 (1993) 474.

- [17] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra, E.K. Hyde, J. Am. Chem. Soc. 75 (1953) 215.
- [18] P. Barnickel, A. Wokaun, Mol. Phys. 69 (1990) 1.
- [19] P. Barnickel, A. Wokaun, W. Sager, H.F. Eicke, J. Colloid Interface Sci. 148 (1992) 80.
- [20] C. Petit, P. Lixon, M.P. Pileni, J. Phys. Chem. 97 (1993) 12974.
- [21] D.E. Sayers, B.A. Bunker, Data Analysis in: D.C. Koningsberger y, R. Prins (Eds.), X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES, J. Wiley and Sons, New York, 1988.
- [22] A. Michalowicz, Logiciels pour la Chimie, Soc. Française de Chimie, Paris, 1991.
- [23] A. Traverse, New J. Chem. 677 (1998).
- [24] A.V. Oppenheim, R.W. Schafer, Discrete-Time Signal Processing, Prentice-Hall, 1989.
- [25] J.J. Rehr, R.C. Alberts, Phys. Rev. B 41 (1990) 8139.
- [26] M. Newville, B. Ravel, D. Haskel, J.J. Rehr, E.A. Stern, Y. Yacoby, Physica B 208–209 (1995) 154.
- [27] A.G. McKale, B.W. Veal, A.P. Paulikas, S.K. Chan, G.S. Knapp, J. Am. Chem. Soc. 110 (1988) 3763.
- [28] TADD (Total Access Diffraction Database), based in the PDF-2 (Powder Diffraction File) of JCPDS-ICDD (Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data), Philips, 1990.
- [29] B.D. Cullity, Elements of X-Ray Diffraction, 2nd ed., Addison-Wesley, 1978.
- [30] L.A. Feigin, D.L. Svergrun, Structure Analysis by Small-Angle X-Ray and Neutron Scattering, Plenum Press, New York, 1987.
- [31] A. Gonzalez Penedo, Obtencion y Propiedades Fisico-Quimicas de Particulas de Cobalto Recubiertas con Material No Magnetico por Reacciones Sucesivas en Microemulsiones, PhD thesis, University of Santiago de Compostela, 1997.
- [32] M. Borowski, J. Phys. IV (Paris) 7 (1997) C2-259.
- [33] A.J. Garcia-Bastida, J. Rivas, M. A. Lopez-Quintela, to be published.
- [34] C. Tojo, M.C. Blanco, M.A. López-Quintela, Current Topics Colloid Interface Sci. 4 (2001) 103.
- [35] M. Dippel, A. Maier, V. Gimple, H. Wider, W.E. Evenson, R.L. Rasera, G. Schatz, Phys. Rev. Lett. 87 (2001) 95505.