

COMPLEX CHARACTERIZATION OF MAGNETIC FLUIDS BY MÖSSBAUER SPECTROSCOPY

V. KUNCSE¹, G. SCHINTEIE¹, B. SAHOO², W. KEUNE², D. BICA³, L. VÉKÁS³, G. FILOTI¹

¹National Institute for Physics of Materials, P.O. Box MG 7, 77125, Bucharest-Magurele, Romania

²Fachbereich Physik, Universität Duisburg-Essen (Campus Duisburg), D-47048, Duisburg, Germany

³Romanian-Academy-Timisoara Branch, Center for Advanced and Fundamental Technical Research, Mihai Viteazul Nr. 23, 300223, Timisoara, Romania

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Abstract. Samples of ferrofluids, consisting in ferrite-like nanoparticles coated with double layers of surfactants and dispersed in water were studied by X-ray diffraction and temperature dependent Mössbauer spectroscopy. Information about the particle mean size, the size dispersion and the effective anisotropy constant was obtained for each sample. Different magnetic relaxation processes were observed in dependence on the surfactant layers.

Key words: ferrofluids, Mossbauer spectroscopy, phase composition, magnetic relaxation, anisotropy.

1. INTRODUCTION

A magnetic fluid, also known as ferrofluid, consists in dispersed ferro/ferri-magnetic nanoparticles in a carrier liquid, such as water or oil. Since the discovery of nanofluids, there has been a growing interest in the theoretical and experimental characterization as well as in the specific applications of such complex magnetic systems. In order to obtain a stable dispersion of the nanoparticles in non-polar or polar solvents, the interparticle magnetic interactions are suppressed by specific ways. The dispersion of ferrite-like magnetic particles in water (a polar solvent) can be ensured by coating the particles with a double layer of surfactants (steric repulsions compensate thus the interparticle magnetic interactions). It has been reported that clusters of nanoparticles could be still formed in water-based magnetic fluids due to the non complete canceling of the interparticle interactions. The dimension of the clusters can give a first hint about both the degree of particle dispersion and the strength of the interparticle interactions. Usually, it can be analyzed *via* optical methods (*e.g.*, dynamic light scattering). In spite of the clustering process, the net attractive interparticle interactions (considered as dipole-dipole type) should be quite weak, due to the steric repulsion induced by the double coating layers. In the following, the attractive interactions are considered to induce only perturbations of the main anisotropy energy of the particles.

Ferrite-like nanoparticles in a ferrofluid can magnetically relax by two different relaxation mechanisms: (i) the Néel relaxation which is characterized by the internal reorientation of the magnetization against an internal energy barrier, and (ii) the Brownian relaxation due to the rotational diffusion of the particle in the liquid. The effective relaxation depends on the faster relaxation process. There is no initially known relation between the two specific relaxation times. They depend on many internal parameters as well as on the cluster dimension and are often competing processes. A way to separate the two contributions, for a correct interpretation of the experimental results, is to cut off one of the two components by choosing suitable experimental conditions. For example, the Brownian relaxation can be removed by freezing the magnetic liquid at low temperatures. Temperature dependent Mössbauer spectroscopy can be applied in this situation, providing information on particle phase composition, local structure and symmetry, local magnetic interactions inside the particle and Néel-type relaxation phenomena. This work deals with a complex characterization by low temperature Mössbauer spectroscopy of magnetic fluids consisting of ferrite-like magnetic particles coated with double layers of surfactants and dispersed in water. It also proves that a suitable interpretation of the temperature dependent relaxation phenomena may provide information on the particle size distribution and on the effective anisotropy constant of the particles. The effective anisotropy constant can be seen, for the analyzed systems, as a superposition of the internal anisotropy constant of the particle and a perturbation-like component due to the interparticle magnetic interactions[1]. For the same types of particles with similar size distribution, the effective anisotropy constant could provide information about the interparticle interaction, and hence, on the degree of dispersion.

2. EXPERIMENTAL

Three ferrofluid samples, labeled as S1, S2 and S3, were analyzed by X-ray diffraction and ^{57}Fe Mössbauer spectroscopy at temperatures ranging from 4.2 K to 220 K. Samples S1 and S3 consist of nanoparticles of CoFe_2O_4 (cobalt ferrite) coated by a double layer of myristic acid and oleic acid, respectively, dispersed in water. Sample S2 contains Fe_3O_4 (magnetite) nanoparticles double coated by a layer of myristic acid and dodecyl-benzene-sulphonic acid (DBSA). The X-ray diffractions were obtained in the usual θ - 2θ geometry. The Mössbauer spectra were collected in transmission geometry, by inserting the sample in a liquid-He bath cryostat. A Mössbauer drive system operating in constant acceleration mode combined with conventional electronics and a ^{57}Co (Rh matrix) source of about 50 mCi activity were employed. The spectra were fitted with the powerful NORMOS program, with option for both discrete and continuously distributed hyperfine parameters [2].

3. RESULTS AND DISCUSSIONS

The X-ray diffraction spectra obtained at room temperature are shown in Fig. 1. Reflection planes specific to the spinel structure were evidenced for all samples. For a cubic structure, the linear dependence between $\sin^2\theta$ and $(h^2+k^2+l^2)$,

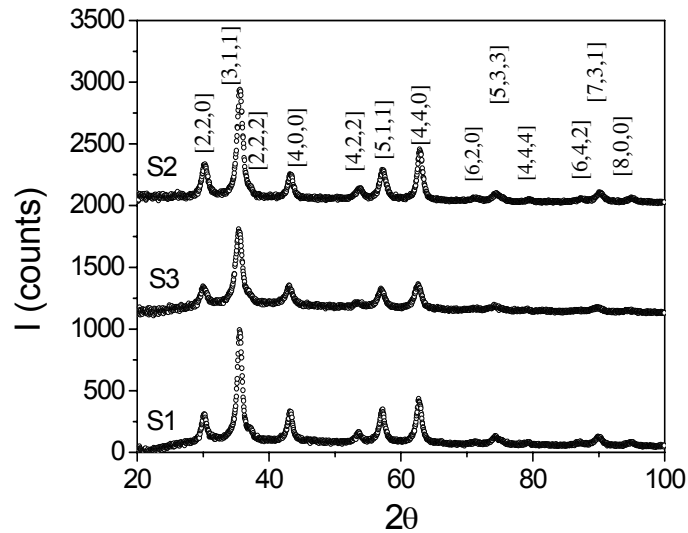


Fig.1 – XRD spectra of the analyzed samples.

with h , k and l the Miller indices corresponding to the diffraction peak at angle θ , was used. The lattice parameter calculated from the slope of this dependence is 0.845(1) nm for sample S1, 0.840(1) nm for sample S3 and 0.838(1) nm for sample S2, suggesting a well crystallized phase. The mean coherence length (supposed to approximate the nano-particle mean size) was obtained *via* the Scherrer formula from the slope of the linear dependence of $\Delta W \cos\theta$ versus $\sin\theta$ (Fig. 2), with ΔW the linewidth of the diffraction peak at angle θ [3]. Quasi-spherical particles were considered, as proved by previous transmission electron microscopy images, previously obtained on similar samples. The instrumental broadening effects were neglected, based on the fact that line-widths obtained on bulk compounds are more than one order of magnitude lower than the corresponding line-widths in the analysed samples. Insignificant slopes were obtained for these linear dependencies, proving almost no strain contributions to the diffraction line-widths.

Mean structural coherence lengths (which approximate the diameter of the magnetic particle) of 11(1) nm were derived for all samples.

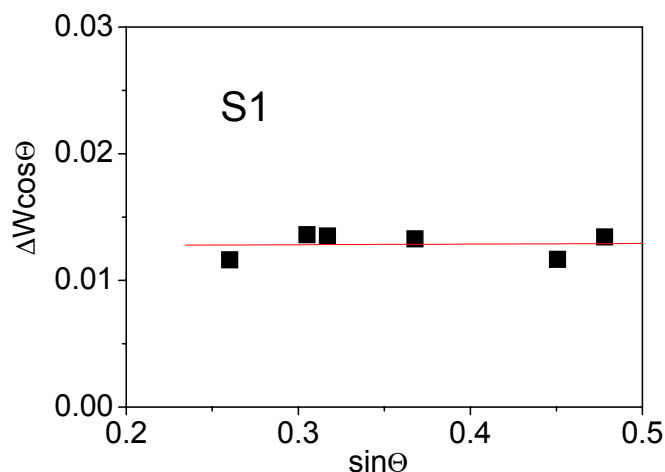


Fig. 2 – The dependence of $\Delta W \cos \theta$ versus $\sin \theta$ for sample S1.

The Mössbauer spectra acquired at different temperatures for sample S3 are shown in Fig. 3. Similar dependences of the Mossbauer spectra versus temperature were also obtained for samples S 1 and S2. Even at the lowest temperature (4.2 K) where magnetic relaxation effects should be completely suppressed, the spectrum consists of a broad sextet, suggesting magnetic order inside the nanoparticle and distributed Fe sites, as is usually observed in fine particles. The mean magnetic hyperfine field at low temperature is about 51.9 T for all the three analyzed samples, close to typical hyperfine fields in magnetite or Co ferrites. Except for the fitting procedure with distributed Fe positions, the 4.2 K Mössbauer spectra can be suitably fitted by two strongly overlapping crystalline sextets with hyperfine fields of about 50 T and 52 T, respectively. The relative areas of the two sextets are close to 50%-50% in samples S1 and S3 and to 36%-64% in S2. It is well known that magnetite is an inverse (or partially inverse) spinel, with majority of Fe^{3+} ions in tetrahedral sites, and Fe^{2+} and Fe^{3+} ions in octahedral positions. Fe^{2+} sites give rise to the sextet with a lower hyperfine field, whereas the double amount of Fe^{3+} sites give rise to the sextet with the higher hyperfine field[4]. This is in agreement with an almost 1/2 relative occupation suggested by the fitting of the Mossbauer spectra of sample S2 with crystalline sextets. On the other side, Co ferrite is an inverse spinel with an equal amount of Fe^{3+} on both octahedral and tetrahedral positions, in agreement with the 1/1 occupation from Mössbauer spectra of sample S1 and S3 (within the fitting procedure with crystalline sites). However the fitting procedure with Fe distributed sizes is more convenient for the interpretation of the magnetic relaxation processes taking place in such systems.

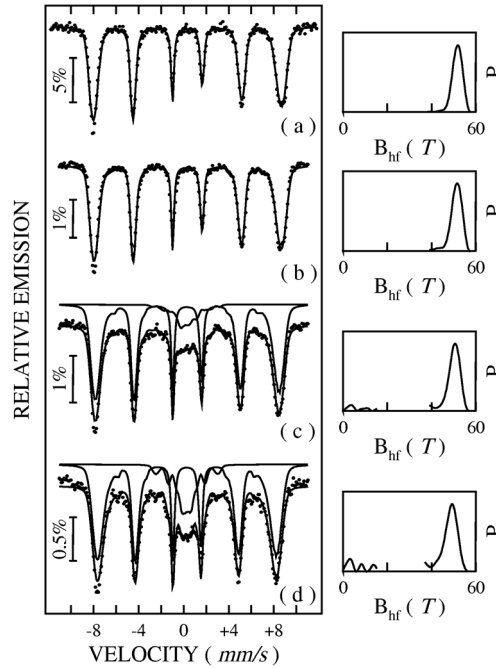


Fig. 3 – Mössbauer spectra of sample S3, acquired at 4.2 K (a), 80 K (b), 126 K (c) and 180 K (d). The corresponding distributions of probability for the hyperfine magnetic field are shown on the right side.

The magnetic anisotropy energy of a spherical magnetic particle of volume V is given by the product KV , where K is the anisotropy energy constant. For fine particles (of mean dimension less than 20 nm) the anisotropy energy is comparable with the thermal energy kT , with k the Boltzmann constant and T the temperature of the system. The thermal fluctuations can be divided into two regimes[5-7]. The first regime (known as the regime of the collective excitations) is characterized by the condition $kT/KV < 0.1$. The coupled spins of the particle oscillate along the easy axis of anisotropy. In a first approximation, the time averaged magnitude of the Fe spin, and hence, of the Fe magnetic hyperfine field, is given by $B_{hf} = B_0[1 - (1/2)(kT/KV)]$. The second regime (known as the regime of superparamagnetic relaxation) is characterized by the condition $kT/KV \leq 0.1$. In this case the thermal energy is high enough to switch the coupled spins of the particle between opposite directions along the easy axis. It results in a fast decrease of the time averaged Fe spins, and hence of the Fe magnetic hyperfine field, down to zero when the thermal energy overpasses the anisotropy energy. The temperature related to such a condition is named the blocking temperature and its experimental knowledge gives

an opportunity for approaching either the particle size (when the anisotropy constant is known) or the anisotropy constant (when the particle size is known). However, the general aspect of the Mossbauer spectra presented in Fig. 3 suggests that mainly the regime of collective excitations is appropriate for the temperatures involved. It can be observed that the hyperfine field distribution shifts to lower hyperfine fields, and the width of the main peak becomes larger, when increasing the temperature. These trends were interpreted as due to dynamic relaxation effects. A similar behavior of the hyperfine field distribution was observed for samples S1 and S2. Above 80 K, a second less intense central component is observed in the Mossbauer spectra as developing from the low temperature sextet. It was interpreted as due to a fraction of superparamagnetic particles. This result could indicate a bimodal type of size distribution for the magnetic nanoparticles, with a much less intense peak of low size (between 8 to 15% relative contribution, depending on the sample). Assuming a blocking temperature of about 100 K and an anisotropy constant of order of 10^4 J/m^3 , the dimension of particles belonging to this peak is of the order of 3-4 nm. For the rest of particles belonging to the main lobe (mean particle size of 11(1) nm and magnetic behavior in the regime of collective excitations), the above relation giving a linear decrease of the hyperfine field *versus* temperature can be exploited [8]. The first derivative of this relation led to a linear relation between the distribution width and the relative volume dispersion, dV/V . A linear increase of the distribution width *versus* the size dispersion dD/D was finally obtained within the usual assumption of a cubic dependence between the particle volume V and its size D . The size dispersion and the effective anisotropy constant were obtained for all analyzed samples from the slopes of the two mentioned dependencies. Whereas the size dispersion seems to be similar within the error bars for all samples (dD/D is about 0.24(2)), the effective anisotropy constant is $2.6(2) \times 10^4 \text{ J/m}^3$, $2.1(2) \times 10^4 \text{ J/m}^3$ and $1.9(2) \times 10^4 \text{ J/m}^3$ for samples S1, S2 and S3, respectively. The obtained anisotropy constant in magnetite particles is twice larger as compared to that of bulk magnetite, while the anisotropy constant of Co ferrite particles is around one order of magnitude lower than one for the bulk. Therefore it is obvious that the double coated surfactant layers play a significant role for the anisotropy constant of the nanoparticles in magnetic fluids and might impose the specific magnetic behavior.

2. CONCLUSIONS

A complex magnetic and structural characterization of the fine particles in ferro-fluids was performed mainly *via* temperature dependent Mössbauer spectroscopy but also using complementary techniques. The distribution of the Fe on different crystallographic sites was determined from low temperature spectra, in the static regime.

Both the size dispersion and local magnetic interactions were obtained from the behavior of the Mössbauer spectra function on temperature. Directly derived from the effect of surfactant layers, large changes of the anisotropy constants on various coated oxide nanoparticles were observed.

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