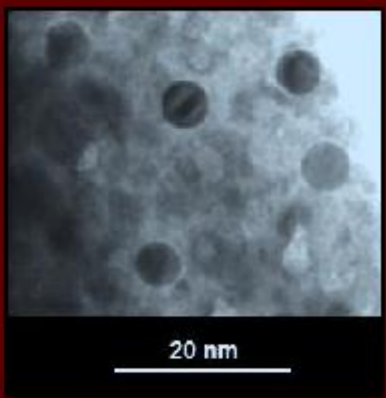
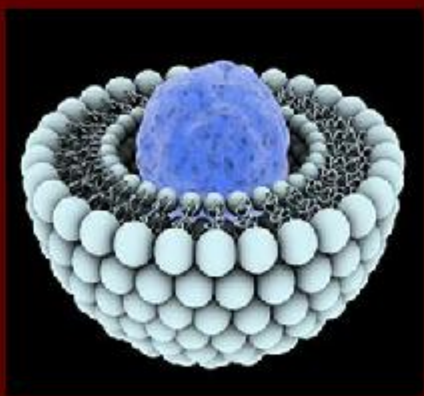
ASSOC. PROFESSOR COSTICĂ CAIZER, PhD

HABILITATION THESIS

SUMMARY

Magnetic properties of ferrimagnetic nanoparticles and nanocomposites with application in bionanotechnology





- 2015 -

ASSOC. PROFESSOR COSTICĂ CAIZER, PhD

HABILITATION THESIS

SUMMARY

Magnetic properties of ferrimagnetic nanoparticles and nanocomposites with application in bionanotechnology

- 2015 -

Imagini copertă:

Nanoparticule de ferită Ni-Zn în matrice de silice amorfă (nanocompozit ferimagnetic) (C. Caizer, in: M. Stefanescu, C. Caizer, *et. al*., Acta Mater., 54 (2006) 1249; © Acta Materialia Inc. Published by ELSEVIER);
Nanoparticulă încapsulată în lipozom (C. Caizer, Bioelectromagnetism, Ed. Eurobit, Timişoara, 2013; © CNRS Photothèque/SAGASCIENCE/CAILLAUD François).

TABLE OF CONTENTS

SUMMARY (7)

CHAPTER I. Professional, scientific and academic achievements (11)

I.1. Scientific achievements (11)

I.1.1. Scientific results obtained and published in ISI papers (13)

I.1.1.1.Temperature dependence of saturation magnetization of $Mn_{0.6}Fe_{2.4}O_4$ nanoparticles surfacted with oleic (13)

I.1.1.2. Magnetic relaxation in nanoparticles systems (21)

I.1.1.2.1.The effect of the amplitude of magnetic field on the thermal relaxation of magnetization in systems of aligned surfacted Fe_3O_4 nanoparticles (21)

I.1.1.2.2.The relaxation/stability of magnetization in Co ferrite nanoparticles dispersed in amorphous silica (33)

I.1.1.3. Magnetic anisotropy of the $(Zn_{0.15}Ni_{0.85}Fe_2O_4)_\gamma$ nanoparticles embedded in $(SiO_2)_{(1-\gamma)}$ ($\gamma = 0.15$) amorphous matrix (42)

I.1.1.4. Magnetic properties of $x(Ni_{0.65}Zn_{0.35}Fe_2O_4)/(100-x)(SiO_2)$ ($x = 5 – 65\%$) ferrimagnetic nanocomposites obtained through the hybrid sol-gel method (50)

I.1.1.5. Magnetic behavior of $Co_\delta Fe_{3-\delta}O_4$ ($\delta = 0.02 – 1.5$) nanoparticles synthesized by complex combinations decomposition method (72)

I.1.2. Achievements in scientific research projects (81)

I.1.3. Directions of scientific research/development (93)

I.1.4. Development/founding of laboratories for scientific research (94)

I.1.5. Published scientific books (95)

I.1.6. International visibility/recognition of scientific achievements (102)

I.2. Professional and academic achievements (105)

I.2.1. Professional and academic evolution (107)

I.2.2. Academic achievements (108)

I.2.3. Courses published (110)

I.2.3. Professional training programs (120)

CHAPTER II. Evolution and development plans of the professional, scientific and academic career (121)

II.1. Evolution and development plans of the scientific career (121)

II.1.1. The issue of future scientific research (121)

II.1.2. Future scientific research/development directions (125)

II.1.3. The development/founding of scientific research laboratories/centers (126)

II.1.4. Books/chapters in books/reviews/ISI publications (127)

II.1.5. Invited scientific conferences (128)

II.1.6. Sustainable collaborations/partnerships in scientific research (128)

II.1.7. Participation in scientific research projects as director (128)

II.1.8. Organizing prestigious national/international scientific conferences, workshops, summer schools (129)

II.2. Plans of evolution and development of the professional and academic career (130)

II.2.1. Development of the professional and academic career (130)

II.2.2. Future directions of teaching (130)

II.2.3. Development/founding of didactic laboratories (130)

II.2.4.The design and implementation of new laboratory works (130)

II.2.5. The courses to be published in the near future (131)

II.2.6. Developing/founding master's degree (131)

II.2.7. Didactic summer schools (131)

II.2.8. Didactic improvement programs and didactic mobility (131)

CHAPTER III. References (133)

ANNEX. List of papers, including those from the scientific research projects coordinated as director, from the postdoctoral period (161)

Annex I. The law in $T^{3/2}$ for saturation magnetisation variation with temperature of $Mn_{0.6}Fe_{2.4}O_4$ nanoparticles surfacted with oleic acid (175)

Annex II. The threshold field and measurement time in the case of magnetic relaxation in aligned nanoparticles, in high alternating (harmonic) magnetic field (182)

Annex III. The ferrimagnetic resonance spectrum (FMR) of $(Zn_{0.15}Ni_{0.85}Fe_2O_4)_{0.15}/(SiO_2)_{0.85}$ nanocomposites (185)

SUMMARY

The habilitation thesis contains my professional, scientific and academic achievements obtained in postdoctoral period, systematized by thematic directions and future evolution and development plan of my carrer. First, my scientific achievements that reflects the research results obtained in my field of interest, more precisely *the magnetic properties of the advanced ferrimagnetic nanomaterials (ferrimagnetic nanoparticles, nanocomposites, nanofluids, ferrimagnetic bionanoparticles/bionanocomposites, with application in bionanotechnology*), are presented. The results were also published in ISI Thomson Reuters-Web of Science papers with an impact factor (ISI) until 4.293 and relative influence score (RIS) until 10.440.

The systematic study of the magnetic properties of these magnetic nanosystems (magnetic behaviour in external field and with temperature, the variation of magnetic measures of interest with nanoparticles size, the relaxation/stability of magnetization, super paramagnetism etc.) with great applicative potential in nanotechnology and bionanotechnoloy, started during my PhD research and continued after 2003 with the contributions brought for this domain development, also partially presented in this habilitation thesis. Nowadays, acknowledgement of the magnetic properties of nanomaterials is an issue of great scientific interest in fundamental research as well in applicative research, due to their properties which are different from those of the corresponding bulk material. This opens *new research directions in this field,* with *great applicative potential*.

The ferrimagnetic nanosystems whose magnetic properties were studied (partially) during postdoctoral period were: *spinel ferrite nanoparticles*, *surfacted* or *not*, *soft* or *hard* magnetic (e.g. Fe_3O_4, $(Ni,Zn)Fe_2O_4$, $(Mn,Fe)Fe_2O_4$, $Co_\delta Fe_{3-\delta}O_4$), dispersed in different matrices: solid (silica matrix $(x(Ni_{0.65}Zn_{0.35}Fe_2O_4)/(100\text{-}x)(SiO_2))$ –*nanocomposites*, liquid (kerosene (Fe_3O_4, $Mn_{0.6}Fe_{2.4}O_4$) – *nanofluids*), air ($Co_\delta Fe_{3-\delta}O_4$) – *dispersed nanoparticles*).

A first issue studied was the one referring the saturation magnetisation of *surfacted nanoparticles*, respectively *its variation with temperature* in the case of nanoparticles of manganese ferrite, surfacted with oleic acid. In the present thesis are shown the results of the variation of reverse initial magnetic susceptibility with temperature of the studied nanosystem, in the temperature range corresponding superparamagnetic behavior (SPM), which validates the deviation from Bloch's law at low temperatures experimentally observed in this case. The deviation of magnetic susceptibility of nanoparticles from Curie-Weiss' law, well-known for the case of bulk material, at temperature decrees in SPM range, was attributed to the increasing magnetic diameter of nanoparticles at temperature decrees as a consequence of the modification of superexchange interaction in the *surface layer of surfacted nanoparticles* (a layer where the magnetic moments are in a different structure from that inside of the nanoparticles, where they are ferrimagnetic aligned).

The Néel stability/relaxation of magnetisation in nanoparticles was studied in the case of a ferrimagnetic material with high magnetocrystalline anisotropy, such as cobalt ferrite, using for this $CoFe_2O_4$ *nanoparticles* with a usual mean diameter of ~10 nm, well isolated between

them by embedment into a silica (amorphous) matrix (in the absence of magnetic dipolar interactions and/or Van de Waals). Using the single-domain particle model, was shown that the nanoparticles magnetisation was *stable* and *uniform* within a very wide range of values, respectively 7.6 – 162 nm, and that the minimum value (limit) of the nanoparticles diameter, from which the magnetisation is stabile for more than 5 years at room temperature, is that of 12.5 nm.

The amplitude of the external magnetic field, used for the magnetization of nanoparticles systems, in the presence of thermal fluctuations/activations of magnetisation, has a great influence upon magnetic moments relaxation. In this thesis is presented an experimental study regarding this aspect, when the magnetic field is alternating (harmonic) of high amplitude and applied along a direction of easy magnetisation of a system of surfacted Fe_3O_4 superparamagnetic nanoparticles, previously *aligned* in the direction of the field, by embedding them in a solid matrix. The remanence ratio of nanosystem experimentally registered in this case, can be explained on the basis of the potential function model and Néel's relaxation time, respectively of measurement time (in the presence of the field), which strongly depend on the magnetic field strength, as long as this is higher that a certain limit value (*threshold* field). The blocking temperature of the magnetic moments, of great practical value (often used for volume or the constant of magnetocrystalline anisotropy of nanoparticles determination) is analyzed in these conditions, being dependent, at a fixed frequency, on the field amplitude and its threshold value. The measurement time (period of time in which can be observed/registered the processes of magnetic relaxation) in the mentioned conditions (dynamic) is always lower than the period of the alternating magnetic field when the amplitude of the magnetic field is higher than the threshold value, and becomes equal with the period only when the amplitude is low (lower or almost equal with the threshold value), the well-known case.

Another aspect of great interest in the case of magnetic nanosystems (nanoparticles, nanocomposites etc.) is the magnetic anisotropy, which in most cases proven to be higher or much higher, on case-to-case basis, than that of magnetocrystalline corresponding to the same material but bulk (single-crystall of large size). Thus, an accurate evaluation of the constant of magnetocrystalline anisotropy in the case of nanoparticles is a problem of major interest in order to correctly understand/explain the high anisotropy in different nanosystems. This problem was studied with ferrimagnetic resonance (FMR) (which permits accurate determinations) in the case of Ni,Zn nanocomposites, formed by spherical nanoparticles of $(Zn_{0.15}Ni_{0.85}Fe_2O_4)_\gamma$ with a diameter of 11.6 nm, embedded (fixed) in an amorphous matrix of $(SiO_2)_{(1-\gamma)}$, for $\gamma = 0.15$ (in the absence of interactions).Taking into account the randomly orientation of the easy magnetisation axes (in the case of nanoparticles dispersed in a silica matrix), it was determined the constant of uniaxial magnetic anisotropy, starting from the Raikher-Stepanov model for the resonance field in the absence of thermal fluctuations on Larmor precession, by finding a value higher than the constant of magnetocrystalline anisotropy of $Zn_{0.15}Ni_{0.85}Fe_2O_4$ bulk ferrite. It was shown that the high magnetic anisotropy of the embedded nanoparticles in the silica matrix it's caused by the existence of a surface anisotropy of which constant of anisotropy is higher with approximate one order of magnitude than the one magnetocrystalline.

The magnetic properties of $x(Ni_{0.65}Zn_{0.35}Fe_2O_4)/(100-x)(SiO_2)$ nanocomposites, at room temperature, obtained (in partnership) by hybrid sol-gel method (the original method), and formed of spherical nanoparticles of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ ferrite, as the only *single* crystalline phase from the system, dispersed quasi-homogeny in the silica matrix's pores, were studied in detail based on the ratio of ferrite/SiO_2 (x = 5 – 65%, % percentage by mass) and the annealing temperature (T) (500 – 1000 ^oC) used at crystallization. Magnetic properties can be controlled by x and T parameters, in the same conditions of synthesis, which lead to different sizes of the nanoparticles (mean diameters in the field ~2 – 39 nm), with a narrow distribution, obtaining a magnetic behaviour of the nanocomposites in external magnetic field, from ferrimagnetic (FM) (with hysteresis), un-hysteretic, until superparamagnetic (SPM, described exactly by Langevin function). Thus, based on the results obtained, the magnetic properties of nanocomposites can be previously tailored depending on the intended purpose. The magnetic behaviour at room temperature and the variation with x and T of the macroscopic magnetic observable of practical interest (saturation magnetisation, coercive field) were explained in relation with the nanoparticles diameter.

Besides fundamental studies, targeting applications in bionanotechnology (nanomedicine) of these nanoparticles, were also prepared (in partnership) $Co_\delta Fe_{3-\delta}O_4$ nanoparticles for δ = 0.02 – 1.5 (Co ions concentration) through complex combinations method (original) and chemical co-precipitation method (improved). It was aimed to obtain nanoparticles with a magnetic anisotropy for a wide range of values, from *hard* to *soft*, based on Co ions concentration. By using the first method there were obtained large nanoparticles, with a mean diameter of > 10 nm (~10 – 43 nm), and by the second method, small nanoparticles with a mean diameter of < 10 nm (~ 2.4 – 10.2 nm). The magnetic properties of the nanoparticles system obtained were studied according to the cobalt ions concentration, crystallization temperature (300 – 1000 ^oC) and nanoparticles size.

The above mentioned issues were partially addressed also in two scientific research projects, a CNCSIS A grant (2006-2008) and a PN-II project, D7 (2007-2010) partnerships, coordinated by me as a director, which are summarized in the present thesis. Within the second project, an almost complete study was made regarding the magnetic behaviour of the nanoparticles system of $Co_\delta Fe_{3-\delta}O_4$ (δ = 0.02; 0.2 – 1.5) ferrite, surfacted/nonsurfacted, in low (susceptibility), moderated and high (until 10,000 Oe) magnetic fields, both in static/quasistatic regime (until 50 Hz) and also dynamic regime (25 Hz – 1 kHz, 20 kHz – 2 MHz), at room temperature, but also at high temperatures (700 – 800 ^oC), and also between 30 – 50 ^oC, in terms of practical application in medicine. Also, it was taken into account the possibility of using $Co_\delta Fe_{3-\delta}O_4$ nanoparticles, *biofunctionalized*, in cancer therapy with high frequency of appearance and mortality (e.g. breast cancer), by magnetic hyperthermia (MHT). When using biocompatible nanoparticles by embedment in liposomes/cyclodextrins, in MHT applications for malign tumor therapy, the large size nanoparticles are suitable for *extracellular* therapy, and the small size ones in *intracellular* therapy (small nanoparticles can easily penetrate cells, destroying them more efficiently from inside out). When using nanoparticles with a mean diameter < 7 nm, hyperthermia can be obtained through superparamagnetic relaxation (SPMHT), being a more efficient way in terms of specific absorption rate (SAR); also, small nanoparticles are better tolerated by living organism because of their reduced toxicity.

Further on, in order to increase SAR, besides these nanoparticles I will also consider the use of nanoparticles based on Fe superparamagnetic oxides, SPION (Super-Paramagnetic Iron Oxide Nanoparticles), like the ones studied so far (Fe_3O_4, $(Ni,Zn)Fe_2O_4$, $(Mn,Fe)Fe_2O_4$ or γ-Fe_2O_3), which are suitable for this type of experiment. All of these are still subject of some inter- and multidisciplinary researches, which I have also recently proposed in a European research project (HORIZON 2020 – ERC-CoG-2014).

In the present thesis there are also shown other achievements during my scientific activity, such as the developed research directions, the development/founding of research laboratories equipped with advanced research installations, the published books, and also the international visibility/recognition of my scientific results (by citations in ISI Web of Science, invitations to be a scientific referee for ISI journals (with ISI until ~8), invitations to be a member of different prestigious international associations/societies professional/scientific, awards etc.).

The academic component of my activity is summarized by my evolution and academic achievements, published courses, training programs coordination.

In the second part of the thesis, the proposed plans for further development of my career in two directions: scientific and academic are presented.

The evolution and development plans of my scientific career include: future scientific research issues, future scientific research/development directions, development/founding of scientific research laboratories/centers, sustainable collaborations/partnerships in scientific research, participation in scientific research projects as director, invited scientific conferences, future books/chapters in books/reviews/ISI papers, organization of prestigious national/international scientific conferences, workshops and summer schools.

The evolution plans of my professional and academic career include: development of my academic and professional career, future teaching directions, development/establishment of teaching laboratories, design and implementation of new laboratory works, courses to be published in the near future, developing/founding master’s degree, didactic summer schools and programs of didactic improvement and didactic mobility.