I.1. ***Intermediary Scientific Report (Summary)***
regarding the implementation of the project from start until present
(September 2013 – December 2014)

Project PN-II-ID-PCE-2012-4-0470
„***Interphase Exchange Coupling in Hard/Soft Magnetic Nanocomposites***"

In the following we will present a summary of the *Intermediary Scientific Report regarding the implementation of the project from start until present (September 2013 – December 2014)*

Contents of the Extended Report

I. Project Objectives

1. The first objective focuses on the elaboration and study of ***new hard and soft magnetic phases*** with remarkable magnetic properties, aiming to optimize the interphase exchange coupling, resulting in exchange coupled magnets, spring magnets, with high remanence and coercivity. This objective will be fulfilled by 3 work packages.
2. The second objective, the main objective of the project, aims at developing ***exchange coupled hard/soft magnetic nanocomposites*** with a high energy product, obtained through mechanical milling or quenching, using hard phases such as $SmCo_5$, $Nd_2Fe_{14}B$, $Sm_2Fe_{17}N_x$ or the newly obtained hard phases and soft phases based on Fe or Fe-Co alloys. The interphase exchange coupling leads to the whole composite behaving like a single hard magnetic phase. This objective will be fulfilled by another 3 work packages.

I.1. Specific Objectives of the 2013 Phase

1. Soft magnetic phases with high magnetization values.
2. Hard magnetic phases with low rare earth content of the *R-M-A* type (*R* = rare earth, *M* = 3*d* transition metal, *A* = metalloid) with high anisotropy and coercivity.
3. Hard/soft nanocomposites with good coercivity and with remanence values higher than those of the hard phases.

I.2. Specific Objectives of the 2014 Phase

1. Hard magnetic phases with low or no rare earth content with high anisotropy and magnetization.
2. The study of the strength of the interphase exchange coupling as a function of the composition, structure and microstructure of the magnetic nanocomposites.
3. Project management and acquisition of materials and equipment.

II. Summary

II.1. Phase 1 Summary (September 2013 – December 2013)

As we have shown in the project proposal, some of the research contained in this project is performed in collaboration with our national or international partners. Even though the financing of the project started in September 2013, thanks to the support of our European partners (University of Rouen and Louis Néel Institute in Grenoble) we have managed to start the research work earlier, and as a result, the obtained results were already presented at international conferences and workshops or published in scientific journals [17, 22, 23, 37]. Furthermore, a PhD thesis on the project topic was finalized on December 19th 2013 [1]. Starting from the assumed objectives and proposed research activities, the studies performed during the project phase correspond to the objectives of the first phase and can be summarized as follows:

- The elaboration of new hard magnetic phases of the *R*-Co-*M* type (*R* = rare earth, *M* = transition metal) and MnAl alloys doped with Ni. The structural and magnetic characterization along with the study of the influence of metalloid and Ni doping, respectively, on the electronic structure [1].
- Effect of milling and annealing conditions on the crystallographic, morphological and magnetic properties of exchange-coupled nanocomposite of the $SmCo_5$/(Fe or $Fe_{65}Co_{35}$) and $Nd_2Fe_{14}B$/α-Fe type [17, 22, 23, 37].
- The investigation of different milling types, milling energies and sample preparation on the interphase exchange coupling [17, 22, 23, 37].

II.2. Phase 2 Summary (December 2013 - December 2014)

Following the assumed objectives, the performed research was focused on studying new hard magnetic phases with low or no rare earth content with high anisotropy and magnetization values and the optimization of the interphase exchange coupling as a function of the composition, structure and microstructure of the nanocomposites. The results can be summarized as follows:

- the study of new magnetic phases $RCo_{5-x}M_x$ type (*R* = Pr, Sm, Tb, Er şi Tm; *M* = Si, Ge, Al, Ga; *x* = 0,5 şi *x* = 1): the elaboration of the compounds, the study of the crystal structure by X-ray (XRD) and neutron diffraction, the study of the electronic structure by XPS, magnetic measurement studies and the study of the magnetic structure through neutron diffraction.

- the elaboration and study of new hard magnetic phases without rare earths of the MnAl type doped with Ni, Ti and Zn: the preparation of the alloys, the study of the magnetic τ-phase stability as a function of composition and preparation (arc and induction melting, quenching, slow cooling) and annealing conditions through XRD, differential thermal analysis and thermomagnetic measurements and the theoretical study of the electronic structure and the determination of the crystallographic positions occupied by the dopant elements: Ni, Ti or Zn.
- In order to determine the influence mechanisms of structure, microstructure and morphology on the interphase exchange coupling in hard/soft exchange coupled nanocomposites, we studied the effect of milling and annealing conditions on the structure and microstructure as well as on the magnetic behavior of the studied nanocomposites as a whole. The milling energy was varied in two ways: a) by modifying the dimension of the milling balls and b) different milling times. The structure and microstructure of the nanocomposite powders was controlled by two annealing types: a) classical annealing at a temperature of 450-650 °C for 0.5-10 h and b) short time annealing at temperatures of 700, 750 or 800°C for 0.5-3 minutes.
- Theoretical calculations were focused on the elaboration of models which could be applied for Bloch or Néel wall movement in magnetic materials. On the other hand, density functional theory calculations in the LSDA+DMFT approximations played an important role in describing the electronic structure of 3*d* transition metals, the dynamic correlations (by means of LSDA+DMFT) determining larger relativistic corrections.

The obtained results were presented at international conferences (invited lectures, oral and poster presentations) [8, 9, 11, 24-27] and published in scientific journals [2, 3, 5, 6, 7, 10, 41].

III. Conclusions and Perspectives

The performed research presented in Chapter III of the extended Scientific Report show the accomplishing of the assumed objectives outlined in Chapter I. A PhD thesis was finalized and defended, the subject being in good agreement with the project objectives regarding the elaboration and study of new hard magnetic phases. The research was focused on the study of new magnetic phases of the $R\mathrm{Co}_{5-x}M_x$ type, the elaboration of the alloys, the study of the crystal structure by XRD and neutron diffraction, the study of the electronic structure through XPS and band structure calculation, magnetic measurement studies and the study of the magnetic structure through neutron diffraction.

The study of new hard magnetic phases without rare earths was undertaken, the research being focused on MnAl-type phases. In order to accomplish this task the crystallographic stability and magnetic properties of the parent $Mn_{50}A_{50}$ and the phases doped with Mn, Ni, Ti or Zn were determined through electronic structure calculations. Experimental studies have shown that the partial substitution of Al with Ni leads to the formation of a second magnetic phase different than the metastable τ phase. We published results obtained on nanocomposites containing soft phases with high magnetization values, such as $Fe_{65}Co_{35}$.

Different milling types were performed in order to optimize the microstructure of the nanocomposites: wet and dry milling, milling at variable energies and shock and friction milling. Regarding the annealing method, two annealing types were chosen: a) a classical annealing for long times at temperatures lower than the recrystallization temperature of the soft phases and b) short time annealing at temperatures higher than the recrystallization temperatures of the hard phases. The magnetic properties of the nanocomposites were studied as a function of the structure and microstructure of the nanocomposite, being one of the main project tasks regarding the enhancement of the interphase exchange coupling. Atom probe tomography gave precious information regarding the interphase diffusion and the evolution of phase composition at the interface. In collaboration with our colleagues at the University of Rouen, for the microstructure and interphase coupling studies on the new hard/soft nanocomposites, we will pay special attention to this research in the next phases. In this sense, for a better understanding and use of interphase diffusion, atom probe tomography studies on short time annealed nanocomposites will be a priority.

Theoretical calculations were focused on the elaboration of models which could be applied for Bloch or Néel wall movement in magnetic materials. On the other hand, density functional theory calculations in the LSDA+DMFT approximations played an important role in describing the electronic structure of 3*d* transition metals, the dynamic correlations (by means of LSDA+DMFT) determining larger relativistic corrections.

Because many of the results contained in the report are under review and not yet published, we have decided that the project website will contain only the results presented at international conferences or results which were already published. The project website address is: http://www.phys.ubbcluj.ro/~viorel.pop/PN-II-ID-PCE-2012-4-0470/pn2.html

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