I.1. ***Intermediary Scientific Report (Summary)***
regarding the implementation of the project from start until present
(September 2013 – December 2015)

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 2015)*

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 19^{th} 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].

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II.3. Phase 3 Summary (16/12/2014 — 31/12/2015)

Considering the three phase objectives, the research was focused on the preparation of new hard magnetic phases and the study of their physical properties as well as on the development of new exchange coupled nanocomposites and the study of their structure, microstructure, and magnetic properties - interphase exchange coupling, remanence, coercivity, and maximum energy product. The third objective was accomplished by ensuring the necessary research management (the team comprises students, Master students, PhD students, technicians, researchers, and teaching staff) and by the acquisition of materials and equipment necessary for the implementation of the project. The scientific results of the present phase can be summarized by looking at the two main research objectives of the project, the third objective referring to project management.

The study of new hard magnetic phases with potential applications in spring magnet-type nanocomposite materials was envisaged. For this objective, two classes of compounds were studied:

- Intermetallic compounds based on the $CaCu_5$ crystal structure. The substitution of Co with Al in $TmCo_5$ leads to a partial replacement of Co 3*g* in the $CaCu_5$ crystal structure. $TmCo_4Al$ is ferrimagnetically ordered having a Curie temperature of 511 K. Due to the different vicinities of Co, the magnetic moments of Co atoms situated on the two distinct crystallographic positions are different. At 2 K, $TmCo_4Al$ shows a strong coercivity, H_c=2,48 T.
- Mn-Al-type or Ce-Co-Mn-type alloys and intermetallic compounds based on Mn. The partial substitution of Co with Mn in $CeCo_2$ preserves the $MgCu_2$-type structure. Ce and Co do not have magnetic moments in these compounds. The magnetic behavior of CeCoMn, $Ce_3Co_3Mn_4$ and Ce_3Co_6Mn is determined mainly by the Mn-Mn interactions. The sign of the magnetic coupling between the Mn ions is dependent on the critical Mn-Mn distance of 2.8 Å: $d_{Mn\text{-}Mn}<d_{crit}$ = antiferromagnetic coupling, $d_{Mn\text{-}Mn}>d_{crit}$ = ferromagnetic coupling. Ce shows an intermediary valence value in $Ce_2Co_{15}Mn_3$, $CeCo_7Mn_5$ and $CeCo_8Mn_4$, where Co and Mn are magnetic. The substitution of Co with Mn leads to a decrease of the ferromagnetic interactions (Co-Co) and the increase of the antiferromagnetic ones (Co-Mn and Mn-Mn). We have shown that Ce_3Co_6Mn has a paramagnetic behavior in the temperature range 4 - 550 K. The $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ alloys are polyphase, the magnetic τ phase being favored by thermal treatments at 470°C, the maximum τ phase concentration values being

76 wt.% and 74 wt.% for $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ respectively. $Mn_{50}Al_{46}Ni_4$ alloys show the presence of the soft magnetic κ phase which has a lower Curie temperature than the hard magnetic τ phase. The spontaneous magnetizations at 4 K are 112 and 106 Am^2/kg for $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ respectively, given by the Mn magnetic moments of 1,11 μ_B/f.u. and 0,92 μ_B/f.u. respectively. Band structure calculations have shown a preference for Ni to occupy the 1*a* and 1*c* Mn positions. The calculated Mn moments were 1,12 μ_B/f.u. and 0,95 μ_B/f.u. respectively, in good agreement with the experimental data. It was shown that the Ni for Mn substitution up to 4 % does not lead to essential changes for the exchange interactions in this system. Milled samples show higher coercivities than bulk ones.

The second objective of the 2015 phase focuses on the soft/hard exchange coupling in $Nd_2Fe_{14}B$/α-Fe nanocomposites. We aimed to optimize the interphase exchange coupling in order to obtain spring magnets with high coercivity, remanence and energy product:

- $(Nd,Dy)_2Fe_{14}B$/α-Fe nanocomposites with 10 or 22 wt.% α-Fe were prepared by mechanical milling and ***two types of thermal treatments*** - classical annealing (550 °C for 1.5 h) and short time annealing at high temperatures of 700-800 °C for times shorter than 3 min. The structure, microstructure and strength of the interphase exchange coupling were experimentally modeled using the milling conditions and the two annealing types. The X-ray diffraction patterns and homogeneity of the chemical composition of the sample particles shows a good homogeneity of the two magnetic phases at the nanometer level. The best magnetic properties were obtained for samples milled for 6 or 8 h. Short time annealing leads to a better crystallinity of the $Nd_2Fe_{14}B$ hard phase and a hampered growth of the Fe crystallites. For all of the composites, the samples with 10 wt.% Fe show the best magnetic properties.
- We have shown the ***importance of milling geometry*** (bowls with Ø = 10 mm or Ø = 15 mm size balls) on the physical properties of $Nd_2Fe_{14}B$+10 wt% Fe nanocomposites. Due to its reduced effect on the crystallinity of the hard $Nd_2Fe_{14}B$, milling with larger diameter balls leads to higher coercivities. This conclusion was based on the comparison of XRD and magnetic data. It was shown that the Fe crystallite sizes can be kept in the 5-20 nm range, dimensions which favor a good hard/soft exchange coupling. Coercive fields up to 0.65 T were obtained, with remanence values of 110 Am^2/kg and $(BH)_{max}$ values of 127 kJ/m^3. The optimization of the magnetic behavior (coercivity, remanence and rectangularity of the demagnetization curve) was discussed taking into account the structure and microstructure of the composite.

The obtained scientific results were presented at international conferences and summer schools (invited lectures, oral or poster presentations) [4, 5, 9-11] and published in scientific journals [1-3, 6-8].

III. Conclusions and Perspectives

III.1. Phases 1 and 2 (September 2013 - December 2014)

The research work performed in the two phases, presented in detail in the Chapter III of the Extended Scientific Report for the period September 2013 - December 2014 show that the objectives of these phases were accomplished. 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.

III.2. Phase 3 (16/12/2014 - 31/12/2015)

The summary of the research results shown in Chapter III of the *Extended Scientific Report* for the period September 2013 - December 2015 has shown that the objectives for this time period have been accomplished. After the finalization of a PhD thesis in 2014, in 2015 a PhD thesis was continued and a new one was started in October 2015. During this phase we focused on the study of new hard magnetic phases with applications in spring magnet-type nanocomposite materials. For this we studied two classes of compounds:

- Intermetallic compounds based on the $CaCu_5$ crystal structure
- Mn-Al or Ce-Co-Mn-type alloys and intermetallic compounds based on Mn.

The second objective was focused on the study of the hard/soft exchange coupling in $Nd_2Fe_{14}B/\alpha$-Fe nanocomposites, where we aimed to optimize the interphase exchange coupling in order to obtain spring magnet materials with high coercivity, remanence and energy product.

The substitution of Co with Al $TmCo_5$ lead to the substitution of Co 3*g* in the $CaCu_5$ crystal structure. $TmCo_4Al$ is ferrimagnetically ordered, having a Curie temperature of 511 K. Due to the different vicinities of Co, the Co magnetic moments on the two distinct crystallographic positions are different. At 2 K, $TmCo_4Al$ shows a high coercivity, H_c=2,48 T.

The partial substitution of Co with Mn in $CeCo_2$ preserves the $MgCu_2$-type structure. Ce and Co do not have magnetic moments in these compounds. The magnetic behavior of CeCoMn, $Ce_3Co_3Mn_4$ and Ce_3Co_6Mn is determined mainly by the Mn-Mn interactions. The sign of the magnetic coupling between the Mn ions is dependent on the critical Mn-Mn distance of 2.8 Å: $d_{Mn-Mn}<d_{crit}$ = antiferromagnetic coupling, $d_{Mn-Mn}>d_{crit}$ = ferromagnetic coupling. Ce shows an intermediary valence value in $Ce_2Co_{15}Mn_3$, $CeCo_7Mn_5$ and $CeCo_8Mn_4$, where Co and Mn are magnetic. The substitution of Co with Mn leads to a decrease of the ferromagnetic interactions (Co-Co) and the increase of the antiferromagnetic ones (Co-Mn and Mn-Mn). We have shown that Ce_3Co_6Mn has a paramagnetic behavior in the temperature range 4 - 550 K.

The $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ alloys are polyphase, the magnetic τ phase being favored by thermal treatments at 470°C, the maximum τ phase concentration values being 76 wt.% and 74 wt.% for $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ respectively. $Mn_{50}Al_{46}Ni_4$ alloys show the presence of the soft magnetic κ phase which has a lower Curie temperature than the hard magnetic τ phase. The spontaneous magnetizations at 4 K are 112 and 106 Am^2/kg for $Mn_{54}Al_{46}$ and $Mn_{50}Al_{46}Ni_4$ respectively, given by the Mn magnetic moments of 1.11 μ_B/f.u. and 0.92 μ_B/f.u. respectively. Band structure calculations have shown a preference for Ni to occupy the 1*a* and 1*c* Mn positions. The calculated Mn moments were 1.12 μ_B/f.u. and 0.95 μ_B/f.u. respectively, in good agreement with the experimental data. It was shown that the Ni for Mn substitution up to 4 % does not lead to essential changes for the exchange interactions in this system. Milled samples show higher coercivities than bulk ones.

$(Nd,Dy)_2Fe_{14}B/\alpha$-Fe nanocomposites with 10 or 22 wt.% α-Fe were prepared by mechanical milling and two types of thermal treatments - classical annealing (550 °C for 1.5 h) and short time annealing at high temperatures of 700-800 °C for times shorter than 3 min. The structure, microstructure and strength of the interphase exchange coupling were experimentally modeled using the milling conditions and the two annealing types. The X-ray diffraction patterns and homogeneity of the chemical composition of the sample particles shows a good homogeneity of the two magnetic phases at the nanometer level. The best magnetic properties were obtained for samples milled for 6 or 8 h. Short time annealing leads to a better crystallinity of the $Nd_2Fe_{14}B$ hard phase and a hampered growth of the Fe crystallites. For all of the composites, the samples with 10 wt.% Fe show the best magnetic properties,

We have shown the importance of milling geometry (bowls with Ø = 10 mm or Ø = 15 mm size balls) on the physical properties of $Nd_2Fe_{14}B$+10 wt% Fe nanocomposites. Due to its reduced effect on the crystallinity of the hard $Nd_2Fe_{14}B$, milling with larger diameter balls leads to higher coercivities. This conclusion was based on the comparison of XRD and magnetic data. It was shown that the Fe crystallite sizes can be kept in the 5-20 nm range, dimensions which favor a good hard/soft exchange coupling. Coercive fields up to 0.65 T were obtained, with remanence values of 110 Am^2/kg and $(BH)_{max}$ values of 127 kJ/m^3. The optimization of the magnetic behavior (coercivity, remanence and rectangularity of the demagnetization curve) was discussed taking into account the structure and microstructure of the composite.

Considering that two PhD students are involved in the research activities proposed in this project, the studies in the next time period will be focused on two main directions: the preparation and study of new hard magnetic systems including anisotropic alloys based on Fe and Fe-Co and the second, and most important objective, the optimization of the interphase exchange coupling through the use of new magnetic phases, in order to prepare new spring magnet-type materials with high coercivity and remanence and the fabrication of magnets through Spark Plasma Sintering (SPS).

The research results were published or presented at international scientific conferences. The PhD students involved in the project participated at two summer schools where they presented posters with the obtained results. The project website, http://www.phys.ubbcluj.ro/~viorel.pop/PN-II-ID-PCE-2012-4-0470/pn2.html, is updated with all of these results.

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