University of Delaware

Final Scientific/Technical Report

High-Energy Permanent Magnets for Hybrid Vehicles and Alternative Energy
Uses

DE-AR0000046

Award:	DE-AR0000046]
Lead Recipient:	University of Delaware
Project Title:	High-Energy Permanent Magnets for Hybrid Vehicles and Alternative Energy Uses
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Contract Administrator:	Geraldine E. Hobbs
Date of Report:	December 23, 2013
Reporting Period:	April 1, 2010 – September 30, 2013

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Public Executive Summary

The research undertaken by a multidisciplinary team consisting of chemists, materials scientists, physicists and engineers from four universities (University of Delaware, University of Nebraska, Northeastern University, Virginia Commonwealth University), Ames National Laboratory and Electron Energy Corporation has been aimed at the development of the next generation high-energy permanent magnets. The concerted efforts were motivated by omnipresence of permanent magnets and strong impact their higher energy density would have had on energy efficiency of existing and future transportation, power generation and energy storage systems.

The principal approach was relied on nanoengineering of advanced permanent magnets by replacing a single magnetic material capable of providing stable ("permanent") magnetic flux with two complementary materials: one responsible for a superior magnetic flux and the other one - for the magnet stability. The novelty we introduced into this "nanocomposite magnet" concept – which is well known theoretically and practically, but never yet produced a superior permanent magnet - was the fabrication of a practical nanocomposite magnet using the bottom up approach- by assembling and consolidating prefabricated nanoparticles of the complimentary materials. Our efforts resulted in further development of the theoretical concept and fabrication principles for the nanocomposites and in synthesis of a range of rare-earth-based hard magnetic nanoparticles intended to support the magnetic flux of the nanocomposite magnets. It is significant that the particle preparation methods (surfactant-assisted ball milling and mechanochemical synthesis) can be scaled up for commercial manufacturing. Because of overwhelming technical difficulties we did not make a breakthrough in the assembly of these flux-supporting particles with separately prepared flux-providing nanoparticles and did not obtain a compact nanocomposite magnet. However, our performed research will help to direct the future efforts, in particular, towards nano-assembly via *coating*, when the two phases which made the nanocomposite are first organized in core-shell-structured particles.

Two other approaches explored in parallel to the principal one were to synthesize (discover) new materials that can be used for both the traditional single-material magnets and the nanocomposite magnets. Integrated theoretical and experimental efforts performed primarily at the University of Nebraska lead to a significant advance in nanocluster synthesis technique and yielded novel *rare-earth-free* nanostructured and nanocomposite materials (although the particular synthesis method used for their preparation cannot be scaled up for commercial manufacturing). Researchers at the Ames National Laboratory examined experimentally fifteen R-Fe-X alloy systems (R = rare earth), which have not been explored earlier due to various synthesis difficulties (high vapor pressure, high reactivity, toxicity, refractory nature). The search did reveal several new ferromagnetic compounds, but none with the magnetic characteristics which might warrant their consideration for permanent magnet applications. Although the research did not yield a breakthrough in permanent magnet, it has made major progress in bottom-up manufacturing of rare-earth-containing nanocomposite magnets with superior energy density and open new directions in development of higher-energy-density

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magnets that do not contain rare earths. The advance in the scientific knowledge and technology made in the course of the project has been reported in 50 peer-reviewed journal articles and numerous presentations at scientific meetings.

Acknowledgements

This research was supported by ARPA-E.

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Accomplishments and Objectives

This award allowed the academia - national lab - industry consortium lead by the University of Delaware to demonstrate a number of key objectives. The focus of the project was on designing high-energy permanent magnets for hybrid vehicles and alternative energy uses.

A number of tasks and milestones were laid out in Attachment 3, the Technical Milestones and Deliverables, at the beginning of the project. The actual performance against the stated milestones is summarized here:

Table 1. Key Milestones and Deliverables.

Tasks	Milestones and Deliverables
Task 1.1: Search for new RE-TM-X compounds	1.1.A.Q1: Identify and hire postdoctoral research assistant (Ames Lab). Actual Performance: (07/01/2010) Decision was made to staff at BS level. Search was initiated and completed and position was filled.
1.1.A. Staffing	1.1.B.Q2: Complete informal report of literature review. Actual Performance: (10/1/2010) Literature review was completed and notebook of phase diagram information prepared.
1.1.B. Determination of selection criteria for ternary element and ranking possible ternary systems in 3 tiers.	1.1.B.Q3: Completed and delivered ranking of at least 15 ternary systems into 3 tiers Actual Performance: (1/1/2011) First tier systems identified.
	1.1.B.Q6: Reevaluate Tier assignments of materials which have not been investigated based on what has been learned in processing highest ranked systems. Actual Performance: (10/1/2011) Tier Three materials were arranged according to atomic radius and previous knowledge of chemically similar elements from previous tiers.
1.1.C. Preparation of ternary diffusion couples for determination of phases existing in a given system	1.1.C.Q1: Complete selection of model system. Actual Performance: (7/1/2010) Nd-Fe-As was selected as model system
	1.1.C.Q2: Complete processing of ternary diffusion couple of the model system. Actual Performance: (10/1/2010) A number of diffusion couple geometries were tried and it was determined that a diffusion couple between Fe and a binary compound produced the best results.

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Tasks	Milestones and Deliverables
1.1.D. Characterization of ternary diffusion couples for determination of phases existing in a given system	1.1.C.Q3: Initiate processing of 2 top ranked tier one materials Actual Performance: (1/1/2011) Processing of Nd-Fe-Ca and Nd-Fe-F was initiated.
	1.1.C.Q4: Complete processing of 2 top ranked tier one materials. Initiate processing of remaining tier one materials Actual Performance: (4/1/2011) Evaluation of the Nd-Fe-F and Nd-Fe-Ca systems has been completed. Samples of remaining Tier One materials were prepared, heat treated and underwent evaluation. Third and final diffusion couple for Nd-Fe-Sr was performed.
	1.1.C.Q5: Initiate processing of Tier Two materials. Actual Performance: (7/1/2011) Processing of Nd-Fe-Bi was initiated
	1.1.C.Q6: Complete processing of Tier One materials. Actual Performance: (10/1/2011) Tier One materials have been processed to our best ability. X = F has already been processed/ isolated to the best of our abilities using industry favored techniques. X = Zn was processed and isolated in near pure form, with a small impurity of ReO by volume.
	1.1.C.Q8: Complete processing of Tier Two materials Actual Performance: (4/1/2012) Multiple experiments were performed producing Fe-rich ternary phase on multi-phase Nd-Fe-I samples, with magnetic transitions measured at 500 K.
	1.1.C.Q9: Initiate investigation of Tier 3 systems. Actual Performance: (6/30/2012) Diffusion couples have been executed for X = S, Mg, Te. Further experiments were performed with the Fe-Nd-S and Fe-Ce-Zn systems, with a new Fe-rich phase measured in the Fe-Ce-Zn system.
	1.1.C.Q11: Submit papers on Tiers 1, 2, 3. Actual Performance: (milestone is not met) Part of the results was presented at a conference in January 2013. The papers on the other findings are in preparation.
	1.1.D.Q3: Complete phase identification in the model system. Actual Performance: (1/1/2011) The single ternary phase in the Nd-Fe-As system was correctly identified.
	1.1.D.Q5: Complete phase identification in the 2 top ranked tier one materials.

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Tasks	Milestones and Deliverables
<p>1.1.E. Preparation of single phase samples of newly discovered ternary compounds which meet the criteria for possible permanent magnet use</p> <p>1.1.F. Characterize single phase samples of new ternary phases</p>	<p>Actual Performance: (7/1/2011) Magnetic transition temperatures and material properties for X=F, Ca found with SQUID and SEM; a new top ranked material, X=Zn, has been added to tier one.</p> <p>1.1.D.Q6: Complete phase identification in the Tier One materials. Actual Performance: (10/1/2011) X = F has already been identified as a metastable phase; X = Zn has been identified as $N_6Fe_{13}Zn$.</p> <p>1.1.D.Q9: Complete phase identification in the Tier Two materials. Actual Performance: (milestone is not met) No phases determined in the Tier Two materials meet the criteria for permanent magnets applications. Subtask 1.1.D was merged with subtask 1.1.C.</p> <p>1.1.E.Q7: Obtain single phase samples of down selected ternary phases found in the 2 top ranked tier one materials (selection criteria: $T_c > 300\text{ }^{\circ}\text{C}$, $4\pi M_s > 13\text{ kG}$, $K_1 > 10^7\text{ erg/cc}$) Actual Performance: (milestone is not met) No phases found meeting the selection criteria.</p> <p>1.1.E.Q8: Obtain single phase samples of down selected ternary phases found in the tier one materials (the same criteria as for Q7) Actual Performance: (milestone is not met t) No phases found meeting the selection criteria. Subtask 1.1.E was merged with subtask 1.1.C.</p> <p>1.1.F.Q8: Characterize single phase samples of down selected ternary phases found in the 2 top ranked Tier One materials. Hand off material(s) with $T_c > 300\text{ }^{\circ}\text{C}$, $4\pi M_s > 13\text{ kG}$, $K_1 > 10^7\text{ erg/cc}$ to EEC and UD for development of sintered magnets and use as a high-H_c phase in nanocomposite magnets. Actual Performance: (milestone is not met) No phases found meeting the selection criteria.</p> <p>1.1.F.Q9: Characterize single phase samples of down selected ternary phases found in the Tier One materials. Hand off material(s) with $T_c > 300\text{ }^{\circ}\text{C}$, $4\pi M_s > 13\text{ kG}$, $K_1 > 10^7\text{ erg/cc}$ to EEC and UD for development of sintered magnets and use as a high-H_c phase in nanocomposite magnets.</p>

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Tasks	Milestones and Deliverables
1.1.G. Investigate processing of candidate compounds into permanent magnets	<p>Actual Performance: (milestone is not met) No phases found meeting the selection criteria. Subtask 1.1.F was merged with subtask 1.1.C.</p> <p>1.1.G.Q10: Produce preliminary permanent magnet samples of down selected ternary phases found in the 2 top ranked tier one materials.</p> <p>Actual Performance: (milestone is not met) No phases found meeting the selection criteria. Subtask 1.1.G was merged with subtask 1.1.C.</p>
<p>Task 1.2: Search for RE-free intermetallics with high anisotropy</p> <p>1.2.A. Staffing</p> <p>1.2.B. Analytical and micro-magnetic modeling</p>	<p>1.2.A.Q1: Q2: Completion of hiring of 3 full or partial FTE research associates/assistants (UNL).</p> <p>Actual Performance: (10/1/2010) Completed the hiring of one postdoctoral research associate and two graduate research assistants.</p> <p>1.2.B.Q2: Identification and reporting of promising RE-free permanent-magnet compounds with $K_1 > 10^7 \text{ erg/cm}^3$, $M_s \geq 15 \text{ kG}$.</p> <p>Actual Performance: (10/1/2010) This analytical and micromagnetic modeling milestone has been achieved by identifying $\text{Co}_{0.9}\text{Pt}_{0.1}$ and $\text{Co}_{0.9}\text{Pd}_{0.1}$ as candidate compounds (the calculated K_1 values are $1.2 \times 10^7 \text{ erg/cm}^3$ and $1.7 \times 10^7 \text{ erg/cm}^3$, respectively; both have M_s of 16 kG).</p> <p>1.2.B.Q4: Calculations of magnetization and anisotropy of strained of Fe/W and other 3d/4d and 3d/5d multilayers</p> <p>Actual Performance: (3/31/2011) Calculations showed that Pd_2Fe_2 and Fe_2Rh may have significant K_1 values of 1 MJ/m^3 and 7 MJ/m^3, respectively.</p> <p>1.2.B.Q6: Micromagnetic determination of optimum morphologies/compositions of core-shell clusters and MnBi-based alloys.</p> <p>Actual Performance: (10/1/2011) Completed via considering the effect of a polymer layer on the hysteresis of hard-soft composites and the effect of additives on the pinning field of domain wall.</p> <p>1.2.B.Q8: Calculations of intrinsic magnetic properties of YCo_5 and HfCo_7.</p> <p>Actual Performance: (3/31/12) The calculations have been performed by using Vienna Ab-Initio Simulation Package supercell calculations.</p> <p>1.2.B.Q9: Micromagnetic modeling of dense core(hard)-shell(soft) nanomagnetic structures.</p> <p>Actual Performance: (6/30/12) Obtained theoretical results for a nanocomposite system of aligned hard regions embedded in a soft</p>

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Tasks	Milestones and Deliverables
1.2.C. Study of Mn-Bi-X1 and layered (Fe-Co)/W system	<p>matrix.</p> <p>1.2.B.Q10: Micromagnetic modeling of HfCo₇/Fe-Co to determine coercivity mechanisms and exchange coupling Actual Performance: (9/30/12) Optimal exchange-coupled nanostructures for HfCo₇/Fe-Co system have been determined.</p> <p>1.2.B.Q11: Micromagnetic modeling (H_c, loop shape) of SmCo₅/Fe-Co and Nd₂Fe₁₄B/Fe-Co nanocomposite magnets. Actual Performance: (12/31/2012) The modeling has been completed.</p> <p>1.2.C.Q4: Measurements on MnBi-X1(X1=Pt,Au), including estimates of H_c, K_1, J_s Actual Performance: (4/1/2011) Results showed that the properties of MnBi are better with Pt than Au. The value of $K_1 = 0.56 \text{ MJ/m}^3$ but the magnetization is low (3.8 kG).</p> <p>1.2.C.Q5: Modified Mn-Bi-X1 alloys chosen for enhancement of PM properties X1=Pt, Au and possibly other 5d elements Actual Performance: (7/1/2011) The values for K_1 and B_c reported in Q4 on MnBi:Pt and MnBi:Au alloys were quite substantial, being in the range 0.2-0.6 MJ/m³ and 2.0-2.1 T, respectively. These are favorable for PM development in the sense of being large and in rare-earth-(RE) free materials, but have the deficiency of containing expensive elements (4.5% in our case) of Pt and Au. For this reason, MnBi:Fe was identified as an excellent system for PM development with no RE or expensive elements.</p> <p>1.2.C.Q6: Mn-Bi-X1 materials with $K_1 = 1 - 10 \text{ Merg/cm}^3$, $J_s = 5 - 10 \text{ kG}$. Determine with EEC and/or UD the potential for development of permanent magnet and use as a high-H_c phase in nanocomposite magnets. Actual Performance: (10/1/2011) The MnBi:Fe + Fe₆₅Co₃₅ material was found to have a theoretical $(BH)_{\text{max}}$ of 56.6 MGOe. This material does have potential as a nanocomposite permanent magnet.</p> <p>1.2.C.Q8: Evaluation of (ε-Co)/W layered systems with 5 - 20% W for magnet development. Actual Performance: (4/1/2012) The findings, along with some related research on Co-W clusters, indicate that Fe-Co/W layered systems are <i>not</i> promising for permanent-magnet development.</p> <p>1.2.C.Q12: Development of magnet fabrication methods.</p>

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	<p>from 0.25 to 0.75.</p> <p>1.2.E.Q9: Investigate nanocomposite $\text{HfCo}_7\text{:Fe-Co}$ and determine K_1, H_c, M_s. Actual Performance: (6/30/2012) Prepared exchange-coupled $\text{HfCo}_7\text{:Fe-Co}$ nanocomposites by co-depositing HfCo_7 nanoclusters and soft Fe-Co phase and determined their K_1, H_c, M_r/M_s, and J_s.</p> <p>1.2.E.Q10: Study magnetic properties (K_1, H_c, M_s) of $\text{YCo}_5\text{:Fe-Co}$. Actual Performance: (9/30/2012) $\text{YCo}_5\text{:Fe-Co}$ nanocomposites were prepared using co-deposition method and characterized. Further work is under progress to understand the coercivity mechanism, and to increase H_c and K_1 of the nanocomposites.</p> <p>1.2.E.Q11: Investigate intrinsic magnetic properties of $(\text{Fe-Co})_{3-x}\text{Z}_x$ ($Z = \text{B, P}$) Actual Performance: (12/31/2012) Co_3B and $(\text{Co,Fe})_3\text{B}$ compounds have been investigated.</p>
<p>Task 1.3: Synthesis of Fe-Co high-magnetization nanoparticles</p> <p>1.3.A. Staffing</p> <p>1.3.B. Synthesis of Fe nanoparticles (UD-Unruh)</p> <p>1.3.C. Synthesis of Fe-Co nanoparticles by a modified polyol reaction (NEU)</p>	<p>1.3.A.Q1: Assemble UD-Unruh and NEU research teams Actual Performance: (7/1/2010) All staffing decisions were made.</p> <p>1.3.B.Q3: 10 g of Fe particles < 30 nm in 100 nm aggregates with $M_s > 175$ emu/g Actual Performance: Subtask 1.3.B was discontinued in July 2011 when all efforts on synthesis of magnetically soft nanoparticles were concentrated at NEU.</p> <p>1.3.C.Q2: $\text{Fe}_{65}\text{Co}_{35}$ particles 10-30 nm, $M_s > 180$ emu/g synthesized via a modified polyol reaction Actual Performance: (10/1/2010) Particles with the required performance (20 - 25 nm, $M_s \approx 200$ emu/g) were obtained for somewhat different composition, around $\text{Fe}_{50}\text{Co}_{50}$.</p> <p>1.3.C.Q4: $\text{Fe}_{65}\text{Co}_{35}$ particles < 25 nm, $M_s > 190$ emu/g, quantity 1 g. Hand off particles to EEC and/or UD for use in nanocomposites. Actual Performance: (4/1/2011) Required size and magnetization values were obtained; nanopowders were handed off.</p> <p>1.3.C.Q6: $\text{Fe}_{65}\text{Co}_{35}$ particles < 25 nm, $M_s > 190$ emu/g, quantity 5 g. Hand off nanoparticles to EEC and/or UD for use in nanocomposite magnets. Actual Performance: (10/1/2011) Required size and magnetization values were obtained; nanopowders were handed off.</p>

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1.3.D. Synthesis of Fe-Co-N nanoparticles by a modified polyol reaction	<p>1.3.C.Q8: 10 g of Fe₆₅Co₃₅ particles < 25 nm, $M_s > 190$ emu/g Actual Performance: (4/1/2012) 10 g batch of Fe-Co nanoparticles 20-30 nm in diameter with $M_s > 195$ emu/g has been produced.</p> <p>1.3.C.Q9: Provide UD regularly with 10 g of Fe-Co nanoparticles (size <25 nm, $M_s > 200$ emu/g. Resolve particle agglomeration issue. Actual Performance: (milestone is not met) Particles with the required nominal properties have been provided. The problem with undesirable agglomeration is not solved.</p> <p>1.3.C.Q10: Attempt to make Fe-Co nanoparticles with size < 20 nm and $M_s > 190$ emu/g. Provide particles regularly to UD (size < 25 nm), $M_s > 200$ emu/g. Actual Performance: (milestone is not met) The problem with undesirable agglomeration is not solved.</p> <p>1.3.C.Q11: Attempt to make Fe-Co nanoparticles with size < 20 nm and $M_s > 190$ emu/g. Provide particles to UD (size < 20 nm). Actual Performance: (12/31/2012) Fe-Co nanoparticles with the size ≈ 27 nm and $M_s > 222.5$ emu/g were obtained in a 10 g batch. These properties are close to the level required. There are, however, difficulties due to undesirable agglomeration of the particles and their deterioration with time.</p> <p>1.3.C.Q12: Attempt to make Fe-Co nanoparticles with size < 20 nm and $M_s > 190$ emu/g. Provide particles regularly to UD (size < 20 nm). Write papers/reports. Actual Performance: (milestone is not met) Although a new sonochemical process yielded the much smaller (5 nm) Fe particles, they were in the low-magnetization amorphous state. The papers has been submitted.</p> <p>1.3.D.Q8: Bcc Fe-Co-N particles 10 - 30 nm with controlled composition Actual Performance: Subtask 1.3.D was discontinued because of unfavorable early results and the need to concentrate efforts on the other approaches.</p>

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Tasks	Milestones and Deliverables
<p>Task 1.4: Fabrication of RE-TM high-coercivity nanoparticles</p> <p>1.4.A. Staffing</p> <p>1.4.B. Fabrication of Nd₂Fe₁₄B nanoparticles by milling / cryomilling</p>	<p>1.4.A.Q1: Assembled UD-Hadjipanayis research team Actual Performance: (6/30/2010) All staffing decisions were made</p> <p>1.4.B.Q2: Nd₂Fe₁₄B nanoparticles by hydrogen decrepitation: size ≤ 500 nm, $M_r \geq 120$ emu/g (75% M_s), $H_c \geq 6$ kOe Actual Performance: (10/1/2010) Although the early milestone had been met, the hydrogen decrepitation approach has been discontinued to concentrate the efforts on more promising techniques.</p> <p>1.4.B.Q6: R-Fe-B particles with size < 100 nm and $H_c = 5$ kOe. Actual Performance: (10/1/2011) The best performance achieved for the R-Fe-B nanoparticles is size < 100 nm, $H_c \approx 7$ kOe, but this H_c value is found via extrapolation of low-temperature measurements.</p> <p>1.4.B.Q8: R-Fe-B particles < 75 nm, $H_c = 7$ kOe. Actual Performance: (milestone is not met) Particles with the mean size 110 nm and $H_c = 15$ kOe were produced by milling MQ3 precursor material. Subsequent milestones for the subtask were modified.</p> <p>1.4.B.Q9: Nd-Fe-B particles with size 200 nm, $H_c > 6$ kOe, $M_r > 100$ emu/g. Actual Performance: (6/30/2012) Nd-Fe-B particles with the average size 130 nm, $H_c = 7.2$ kOe, $M_r = 136$ emu/g were separated via sedimentation in ethylene glycol.</p> <p>1.4.B.Q10: Nd-Fe-B particles with size 100 nm, $H_c > 5$ kOe, $M_r > 100$ emu/g. Actual Performance: (9/30/2012) Nd-Fe-B particles with the average size 115 nm, $H_c = 8.5$ kOe, $M_r = 96$ emu/g were separated via sedimentation in ethylene glycol.</p> <p>1.4.B.Q11: Nd-Fe-B particles with size 100 nm, $H_c > 7$ kOe, $M_r > 120$ emu/g. Actual Performance: (milestone is not met) The size and H_c of Nd-Fe-B particles has not been improved. High M_r of 138 emu/g has been achieved for HDDR precursors, although for the average size of 280 nm.</p> <p>1.4.B.Q12: Nd-Fe-B particles with size 100 nm, $H_c > 7$ kOe, $M_r > 130$ emu/g. Actual Performance: (milestone is not met) The mechanochemical approach yielded Nd-Fe-B particles with M_r of 100 - 112 emu/g and H_c</p>

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Tasks	Milestones and Deliverables
1.4.C. R-Fe-B particles by mechanochemical synthesis	<p>4.5 - 6 kOe.</p> <p>1.4.C.Q6: Prepare by mechanochemical synthesis R-Fe-B samples with correct composition and structure as determined by XRD. Actual Performance: (9/30/2011) Completed. Synthesis of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure through calciothermic reaction has been confirmed by XRD.</p> <p>1.4.C.Q7: Prepare via mechanochemical synthesis R-Fe-B particles with size < 200 nm, $M_r > 75\% M_s$, $H_c = 5$ kOe. Actual Performance: (31/3/2013) Obtained $\text{R}_2\text{Fe}_{14}\text{B}$ particle < 200 nm in size with $H_c = 6.2$ kOe, $M_r > 75\% M_s$. The result was only achieved by Q12.</p> <p>1.4.C.Q9: Particles < 100 nm, $M_r > 0.8M_s$ and $H_c = 10$ kOe. Actual Performance: (milestone is not met) The breakthrough with mechanochemically synthesized $\text{R}_2\text{Fe}_{14}\text{B}$ nanoparticles was made too late, during Q12; by that time, 1.4.C.Q9 and 1.4.C.Q10 milestones were formally removed from the task schedule.</p>
1.4.D. Fabrication of Sm-Co nanoparticles by mechanochemical synthesis	<p>1.4.D.Q4: Sm-Co nanoparticles with $H_c > 10$ kOe before washing. Actual Performance: (4/1/2011) Completed. Sm-Co particles with a size of 30-150 nm and $H_c = 10.8$ kOe were obtained.</p> <p>1.4.D.Q5: Sm-Co particles < 200 nm with $M_s > 60$ emu/g, $H_c > 8$ kOe Actual Performance: (7/1/2011) Sm-Co nanoparticles with the 1:5 and 2:7 structures were made with size down to 150 nm, $M_r = 63$ emu/g and $H_c > 30$ kOe.</p> <p>1.4.D.Q7: Prepare by mechanochemical synthesis washed, separated Sm-Co particles < 100 nm with $M_r > 80$ emu/g, $H_c > 8$ kOe. Actual Performance: (4/1/2012) $\text{Sm}_2\text{Co}_{17}$ powders with mean particle size equal or smaller than 100 nm have $M_r = 64-68$ emu/g and $H_c > 15$ kOe.</p> <p>1.4.D.Q9: Fabricate Sm-Co nanoparticles with a size 100 nm, $H_c > 10$ kOe and $M_r > 85$ emu/g. Actual Performance: (6/30/2012) Prepared $(\text{Sm},\text{Pr})_2(\text{Co},\text{Fe})_{17}$ powders with mean particle size of 93 nm, $M_r = 89$ emu/g, $H_c = 13.8$ kOe.</p> <p>1.4.D.Q10: 5g Sm-Co nanoparticles with $M_r > 100$ emu/g and $H_c > 7$ kOe. Actual Performance: (9/30/2012) Prepared 5.5+ g of $(\text{Sm},\text{Pr})_2(\text{Co},\text{Fe})_{17}$</p>

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Tasks	Milestones and Deliverables
<p>1.4.E. Preparation of Sm-Co alloy powder < 100 nm in size with good magnetic properties via calciothermic reduction</p>	<p>powders with $M_r = 100.5 - 107.8$ emu/g and $H_c = 6.7 - 8.3$ kOe.</p> <p>1.4.D.Q11: Supply 10g Sm-Co particles with a size 100 nm, $M_r > 100$ emu/g, $H_c > 7$ kOe. Attempt to make Sm-Co particles with size below 100 nm Actual Performance: (12/31/2012) Total of 15 g of $(\text{Sm,Pr})_2(\text{Co,Fe})_{17}$ particles were prepared, including 8 g with the nominally required properties. The needs of coating, assembly and compaction experiments have been satisfied.</p> <p>1.4.D.Q12: 10g Sm-Co particles size 100 nm, $M_r > 100$ emu/g, with $H_c > 7$ kOe. Actual Performance: (3/31/2012) Only 4 g was actually produced during Q12, but together with 5 g prepared earlier ahead of the schedule this amount covered all the needs of coating, assembly and compaction experiments.</p> <p>1.4.E.Q5: Prepare 5g lots of precursor nanoparticles with nominal Sm/Co ratios of 1/5 and 2/17 based on the autocombustion method Actual Performance: (6/30/2011) The 5g of precursor nanoparticles were made and after annealing showed an $H_c > 20$ kOe.</p> <p>1.4.E.Q7: Prepare a Sm-Co alloy by calciothermic reduction with H_c in the presence of oxidation products greater than 25 kOe. Prepare a Sm-Co alloy with $H_c > 20$ kOe after the removal of CaO. Actual Performance: (12/31/2011) Prepared SmCo_5 alloy with room temperature $H_c > 50$ kOe in the presence of the by-products of the calciothermic reaction and 22.7 kOe after removal of CaO.</p> <p>1.4.E.Q9: Prepare submicron-sized Sm-Co powder (in the presence of aggregation and grain growth inhibitors such as CaO, NaCl, KCl, or NaCl/KCl) with $H_c > 25$ kOe. Prepare submicron-sized Sm-Co alloy powder with $H_c > 20$ kOe after removal of the aggregation and grain growth inhibitors. Actual Performance: (milestone is not met) Prepared 2-5 μm SmCo_5 particles with (extrapolated) room temperature $H_c > 35$ kOe. The goal of achieving submicron-sized SmCo_5 is being addressed by using a higher energy planetary ball in conjunction with various milling fluids.</p> <p>1.4.E.Q10: Prepare Sm-Co alloy powder < 100 nm in size with $H_c > 20$ kOe after removal of the aggregation and grain growth inhibitors. Actual Performance: (milestone is not met) The average particle size has been reduced to less than 200 nm, but at the expense of</p>

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Tasks	Milestones and Deliverables
	<p>emergence of a soft magnetic second phase. Optimum heat treatment conditions are being sought.</p> <p>1.4.E.Q11: Prepare Sm-Co particles < 100 nm with $H_c > 20$ kOe, $M_r > 75$ emu/g. Provide 10 g of these nanoparticles for the compaction experiments. Actual Performance: (milestone is not met) It was not possible to assure the required level of the magnetic properties in the particles smaller than 1000 nm.</p> <p>1.4.E.Q12: Write report. Provide 10 g of these nanoparticles for the compaction experiments. Actual Performance: (milestone is not met) The research findings were reported at a conference and published in a peer-reviewed journal. No anisotropic nanoparticles were provided for compaction experiments.</p> <p>1.4.F. Fabrication of SmCo₅ nanoflakes by high-energy milling</p> <p>1.4.F.Q4: SmCo₅ nanoflakes with thickness < 100 nm, $M_r > 70$ emu/g, $H_c > 15$ kOe. Actual Performance: (4/1/2011) Required properties have been achieved.</p> <p>1.4.F.Q6: SmCo₅ nanoflakes with thickness < 100 nm, $M_r > 75$ emu/g, $H_c > 15$ kOe. Send 1 g of material to VCU. Actual Performance: (10/1/2011) SmCo₅-based nanoflakes with thickness < 100 nm, $M_r > 75$ emu/g ($4\pi M_r = 8$ kG), $H_{ci} > 15$ kOe have been synthesized by surfactant assisted high energy ball milling.</p> <p>1.4.F.Q8: 5g of flakes with thickness ≤ 50 nm, $M_r \geq 80$ emu/g (75% M_s), $H_{ci} \geq 15$ kOe Actual Performance: (3/31/2012) Large amounts (tens of grams) of nanoflakes with an average thickness of 50- 100 nm have been obtained with $M_r = 77$ emu/g (at no demagnetization correction) and $H_{ci} > 20$ kOe. Upon obtaining these results, subtask 1.4.F, which had been performed by EEC, was discontinued because of the need to concentrate efforts on the other approaches. The major goals of the subtask have been successfully achieved.</p> <p>1.4.G. Fabrication of Sm₂Fe₁₇N_x nanoparticles and nanoflakes by high-energy milling</p> <p>1.4.G.Q4: Sm-Fe-N nanoflakes with thickness < 500 nm, $M_r \geq 70$ emu/g and $H_c \geq 4$ kOe. Actual Performance: (3/31/2011) Sm-Fe-N flakes with the right thickness, $M_r = 75$ emu/g and $H_c = 9.3$ kOe were obtained.</p>

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Tasks	Milestones and Deliverables
	<p>1.4.G.Q5: Sm-Fe-N flakes with thickness < 300 nm, $M_r > 85$ emu/g and $H_c > 5$ kOe. Actual Performance: (7/1/2011) Sm-Fe-N flakes with thickness less than 300 nm, $M_r = 95$ emu/g and $H_c = 7$ kOe were obtained.</p> <p>1.4.G.Q7: Sm-Fe-N flakes with thickness < 200 nm, $M_r > 100$ emu/g, $H_c > 8$ kOe. Actual Performance: (12/31/2011) Prepared Sm-Fe-N flakes with thickness < 200 nm, $M_r = 101.2$ emu/g, $H_{ci} = 11.5$ kOe.</p> <p>1.4.G.Q8: Sm-Fe-N particles < 100 nm, $M_r > 90$ emu/g, $H_c > 7$ kOe Actual Performance: (milestone is not met) The best particles produced so far have a mean size of 490 nm, $M_r = 105.5$ emu/g, $H_c = 9.9$ kOe. Recent experiments using 0.3 mm diameter milling media have produced a slurry mean size of 317 nm, but smaller M_r and $H_c > 7$ kOe. Subtask 1.4.G was discontinued because of unfavorable early results the need to concentrate efforts on the other approaches.</p>
<p>Task 1.5: Fabrication of core-shell composite particles and nanoparticles</p> <p>1.5.A. Staffing</p> <p>1.5.B. Fabrication of Sm-Co powder with submicron particles size by milling (EEC)</p> <p>1.5.C. Coating Sm-Co powders with Fe nanolayers (VCU)</p> <p>1.5.D. Synthesis of samarium nanoparticles using sodium reduction method (VCU)</p> <p>1.5.E. Fabrication of Fe-nanoparticle-coated SmCo_x powders (EEC)</p>	<p>1.5.A.Q1: Assembled research team (VCU) Actual Performance: (6/30/2010) Two first year graduate students were put on RA.</p> <p>1.5.B.Q4: 100 g particles with $M_r = 5 - 8$ kG, particle size ≤ 1000 nm and $H_c = 5 - 10$ kOe. Send powders to VCU. Actual Performance: (4/1/2011) Sm-Co powders with submicron particles size were sent to VCU.</p> <p>1.5.CQ.5: Fe coating on Sm-Co powders, thickness < 25 nm. Hand off coated powders to EEC for characterization and development of nanocomposite magnets. Actual Performance: (7/1/2011) 150 g nanoflake powders were shipped from EEC on June 20, 2011.</p> <p>1.5.D.Q7: Demonstration of successful synthesis of pure Sm particles < 50 nm. Actual Performance: (milestone is not met) Attempts to synthesize Sm nanoparticles were not successful. Early report about successful synthesis was based on incorrect interpretation of the XRD data.</p> <p>1.5.E.Q8: 5g of flakes with thickness ≤ 50 nm, $M_r \geq 80$ emu/g (75% M_s), $H_{ci} \geq 15$ kOe Actual Performance: (3/31/2012) Tens of grams of nanoflakes with an average thickness of 50- 100 nm have been manufactured with $M_r = 77$ emu/g (at no demagnetization correction) and $H_{ci} > 20$ kOe.</p>

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Tasks	Milestones and Deliverables
	<p>1.5.E.Q9: Demonstrate coating of etched Sm-Co flakes. Develop and test reliable characterization protocols. Actual Performance: (6/30/2012) More reliable testing protocol has been developed.</p> <p>1.5.E.Q10: Coated Sm-Co flakes with increased remanence by 10%. Actual Performance: (milestone is not met) It was no significant progress associated with the subtask.</p> <p>1.5.E.Q11: Coated Sm-Co flakes with increased remanence by 20%. Actual Performance: (milestone is not met) An 18.5% increase of the Mr has been documented in one of the SmCo₅/Fe nanocomposites prepared via supercritical-CO₂-assisted mixing. However, this result requires confirmation.</p> <p>1.5.E.Q12: Coated Sm-Co flakes with increased remanence by 25% and $H_c > 8$ kOe. Actual Performance: (milestone is not met) The required properties were not achieved.</p>
1.5.F. Synthesis of Sm-Co hard magnetic nanoparticles	<p>1.5.F.Q10: Demonstration of successful synthesis of SmCo₅ nanoparticles with $M_s > 80$ emu/g, $H_c > 8$ kOe. Hand off nanoparticles to EEC and/or UD for use in nanocomposite magnets. Actual Performance: (milestone is not met) Subtask 1.5.F was discontinued because of unfavorable early results the need to concentrate efforts on the other approaches.</p>
1.5.G. Chemical synthesis of Sm-Co/Fe core-shell nanoparticles (VCU)	<p>1.5.G.Q12: Report on chemical synthesis. Feasibility of synthesis of Nd₂Fe₁₄B nanoparticles. Actual Performance: (milestone is not met) Subtask 1.5.G. was discontinued because of unfavorable early results the need to concentrate efforts on the other approaches.</p>
Task 2.1: Theoretical modeling of exchange-coupled nanoassemblies 2.1.A. Staffing 2.1.B. Updating of simulation programs 2.1.C. Calculation of optimal volume fractions and spatial	<p>2.1.A.Q2: Assembled research team (UD-Chui) Actual Performance: (6/30/2010) Research team has been assembled.</p> <p>2.1.B.Q3: Converted simulation programs which include Nd-Fe-B Actual Performance: (1/1/2011) Programs had been converted, the first simulation results obtained.</p> <p>2.1.C.Q4: Theoretical results on exchange-coupled multilayer systems (different orientations). Actual Performance: (4/1/2011) The energy product was determined in multilayer-type composites of Nd-Fe-B/Fe and Sm-Co/Fe-Co as a</p>

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Tasks	Milestones and Deliverables
<p>arrangements for phases in nanocomposite systems</p> <p>2.1.D. Refinement of system parameters based on feedback from experimental results</p> <p>2.1.E. Examine the effects of cluster shapes, morphology and alignment</p>	<p>function of size, composition and texture.</p> <p>2.1.D.Q5: Refined model, Actual Performance: (7/1/2011) Refined multilayer model based on experimental input.</p> <p>2.1.E.Q6: Theoretical results for platelets. Actual Performance: (10/1/2011) Completed by studying the multilayer composites of Sm-Fe-N and Fe-Co.</p> <p>2.1.E.Q7: Theoretical results for cubes and spheres (different structural arrangements). Actual Performance: (1/1/2012) Studied composites of Sm-Fe-N cubes of random sizes in a FeCo matrix.</p> <p>2.1.E.Q9: Modeling of Sm-Co/Co-Fe multilayers. Modeling of exchange coupled systems, with random orientation. Actual Performance: (3/30/2012) Modeling of multilayered magnetized parallel to the layers has been completed. Modeling of randomly oriented exchange coupled systems has been completed.</p> <p>2.1.E.Q10: Monte Carlo modeling of nanocomposites with graded interface. Modeling of exchange coupled systems, with random orientation. Actual Performance: (9/30/2012) Modeling of graded SmCo₅/Sm₂Co₁₇/Fe-Co and randomly oriented Pr₂Fe₁₄B/Fe systems has been completed.</p> <p>2.1.E.Q11: Propose ideal microstructures with graded properties. Modeling of exchange coupled systems, with random orientation. Actual Performance: (12/31/2012) Modeling of graded SmCo₅/Nd₂Fe₁₄B/Fe-Co has been completed. Modeling of randomly oriented Pr₂Fe₁₄B/Fe systems with a wide range of Fe concentration has been completed.</p> <p>2.1.E.Q12: Write papers. Modeling of exchange coupled systems, with random orientation. Actual Performance: (3/31/2013) Modeling of exchange coupled systems, with random orientation has been completed. The results of the theoretical work on the task 2.1 were published in peer-reviewed journals.</p>

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Tasks	Milestones and Deliverables
Task 2.2: Assembling nanoparticles 2.2.A. Random blending 2.2.B. <i>Self-assembly via surface functionalization</i> 2.2.C. Self-assembly by DNA surface functionalization	2.2.A.Q7: Anisotropic exchange-coupled blends of hard magnetic nanoparticles /nanoflakes and soft magnetic nanoparticles with $4\pi M_s > 8$ kG for Nd-Fe-B-based blends and $4\pi M_s > 6$ kG for Sm-Co-based blends. Actual Performance: (1/1/2012) Powder blends were prepared and the required properties were obtained. 2.2.B.Q9: Anisotropic exchange-coupled blends of hard magnetic nanoparticles/nanoflakes and soft magnetic nanoparticles with $4\pi M_s > 12$ kG for Nd-Fe-B-based blends and $4\pi M_s > 9.5$ kG for Sm-Co-based blends. Actual Performance: (milestone is not met) Achieved the required $4\pi M_s$ values in $\text{Sm}_2(\text{Co,Fe})_{17}/\text{FeCo}$ assemblies. Experiments with Nd-Fe-B-based blends are being delayed by unavailability of adequate quantities of Nd-Fe-B nanoparticles. 2.2.B.Q10: Develop techniques for [2D] assembly of composite structure with ordered distribution of soft phase. Actual Performance: (9/30/2012) The basic condition for functionalization of $\text{Sm}_2(\text{Co,Fe})_{17}$ and Fe(Co) nanoparticles have been successfully established. Partial assembly of the particles has been achieved. 2.2.B.Q11: Develop techniques for [3D] assembly of composite structure with ordered distribution of soft phase. Actual Performance: (milestone is not met) The Q11 efforts were dedicated to functionalization of the Fe(Co) nanoparticles. There was no progress in the assembly of a hard/soft nanocomposite. 2.2.B.Q12: Compact the assembled composite structures. Actual Performance: (milestone is not met) There was no progress in the assembly of a hard/soft nanocomposite. 2.2.C.Q12: Decision on feasibility of DNA surface functionalization. Actual Performance: Subtask 2.2.C has been merged with subtask 2.2.B and milestone 2.2.C.Q12 has been removed from the task schedule.

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Tasks	Milestones and Deliverables
Task 2.4: Development of industrialization plan for the new composite magnets	<p>2.4.Q10: Develop draft industrialization plan for the new composite magnets. Actual Performance: (9/30/2012) Draft industrialization plan for the new composite magnets has been developed.</p> <p>2.4.Q11: Provide final industrialization plan for the new composite magnets. Actual Performance: (milestone is not met) The technology of nanocomposite magnets is not yet ready for commercialization.</p>

Computer modeling, performed in the course of the project at University of Delaware (UD-Chui) consisted in finite-temperature Monte Carlo simulation under periodic boundary conditions. University of Nebraska contributed micromagnetic simulations and supercell electronic structure calculations with Vienna Ab-Initio Simulation Package. All simulation results cited as Accomplishments have been published in peer-reviewed journals.

Project Activities

The project has been focused on obtaining permanent magnet materials with a maximum energy product superior to those of the existing materials, such as Nd-Fe-B, for hybrid vehicles and alternative energy applications. Two out of the three approaches employed in the project relied on the known correlations between a magnet performance and fundamental properties of the material. Thus, sufficiently high values of the Curie temperature, spontaneous magnetization and magnetocrystalline anisotropy served us as the criteria in our search for new high-anisotropy ferromagnetic compounds which was performed separately for 15 never-before-studied R-Fe-X alloy systems (R = Nd, Ce; X = Li, Na, Mg, Ca, Sr, Zn, Cd, Bi, S, Se, Te, F, Cl, Br and I) and for rare-earth-free alloy systems. The third approach relied on the known theoretical concept of a two-phase exchange-coupled nanocomposite magnet; we attempted to utilize this concept to fabricate via the bottom up approach an anisotropic permanent magnet with a significant volume content of a high-magnetization Fe(Co) phase and superior values of the remanent induction and maximum energy product. In summary, several new ferromagnetic R-Fe-X compounds have been discovered, but none of them was found to be suitable for permanent magnets. Significant advancement has been made in the nanocluster synthesis technique which allowed us to develop novel *rare-earth-free* nanostructured and nanocomposite materials, such as crystallographically anisotropic Zr(Hf)-Co and Zr(Hf)-Co/Fe-Co. Also, a significant progress has been made towards the development of a bottom-up-built nanocomposite permanent magnet with the greatest advances having been made in (i) theoretical foundation of practical nanocomposite magnets (with a focus on finite temperature conditions and morphology of the phases, (ii) synthesis of crystallographically anisotropic

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SmCo₅ nanoflakes, (iii) mechanochemical synthesis of crystallographically anisotropic (Sm,Pr)₂(Co,Fe)₁₇ nano-particles and (iv) mechanochemical synthesis of crystallographically anisotropic Nd₂Fe₁₄B nanoparticles.

In July 2011, the tasks and milestones were modified to extend the scope of processing techniques used for manufacturing of hard magnetic nanoparticles. In particular, two new subtasks on mechanochemical synthesis were added to Task 1.4. In July 2012, several more modifications were made in order to drop the less promising subtasks and concentrate the efforts on those with the higher probability of success. The modifications included restructuring of Task 2.3 from compaction-method specific subtasks to material-specific ones, dropping of Tasks 2.4 (Testing of newly developed magnets) and 2.5 (Design high-performance motors with the newly developed magnets), and introduction of a task on the development of industrialization plan for the new composite magnets.

Project Outputs

A. Journal Articles

1. L. Zheng, B.Z. Cui, N.G. Akdogan, W.F. Li, G.C. Hadjipanayis, "Influence of octanoic acid on SmCo₅ nanoflakes prepared by surfactant-assisted high energy ball milling," *Journal of Alloys and Compounds* 504 (2010) 391.
2. B.Z. Cui, L.Y. Zheng, D. Waryoba, M. Marinescu, G.C. Hadjipanayis, "Anisotropic SmCo₅ flakes and nanocrystalline particles by high energy ball milling," *Journal of Applied Physics* 109 (2011) 07A728.
3. L. Zheng, A.M. Gabay, W.F. Li, B.Z. Cui, G.C. Hadjipanayis, "Influence of the type of surfactant and hot compaction on the magnetic properties of SmCo₅ nanoflakes," *Journal of Applied Physics* 109 (2011) 07A721.
4. L. Zheng, B.Z. Cui, G.C. Hadjipanayis, "Effect of different surfactants on the formation and morphology of SmCo₅ nanoflakes," *Acta Materialia* 59 (2011) 6772.
5. A.M. Belemuk, S.T. Chui, "Magnetizing reversal in multilayer hard-soft composites SmCo₅-FeCo," *Journal of Applied Physics* 109 (2011) 07A729.
6. A.M. Belemuk, S.T. Chui, "Coercivity and energy product in multilayer hard-soft composites Nd₂Fe₁₄B - FeCo," *Journal of Applied Physics* 109 (2011) 093909.
7. A.M. Belemuk, S. T. Chui, "Comparative study of finite temperature demagnetization in Nd₂Fe₁₄B and SmCo₅ based hard-soft composites," *Journal of Applied Physics* 110 (2011) 073918.
8. B. Balamurugan, R. Skomski, X.Z. Li, S.R. Valloppilly, J.E. Shield, G.C. Hadjipanayis, D.J. Sellmyer, "Cluster synthesis and direct ordering of rare-earth transition-metal nanomagnets" *Nanoletters*, 11 (2011) 1747.
9. P.K. Sahota, R. Skomski, A. Enders, D.J. Sellmyer, A. Kashyap, "Anisotropy of zigzag chains of palladium," *Journal of Applied Physics* 109 (2011) 07E322.
10. A. Kashyap, P. Manchanda, P.K. Sahota, R. Skomski, J.E. Shield, D.J. Sellmyer, "Anisotropy of W in Fe and Co," *IEEE Transactions on Magnetics* 47 (2011) 3336.
11. A. Kashyap, R. Skomski, P. Manchanda, J.E. Shield, D.J. Sellmyer, "Layered transition-metal permanent-magnet structures," *Journal of Applied Physics* 109 (2011) 07A714.

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12. Y. Liu, T.A. George, R. Skomski and D.J. Sellmyer, "Aligned and exchange-coupled FePt-based films," *Applied Physics Letters* 99 (2011) 172504.
13. P. Kharel, X. Z. Li, V. R. Shah, N. Al-Aqtash, K. Tarawneh, R. F. Sabirianov, R. Skomski, and D. J. Sellmyer, "Structural, magnetic, and electron transport properties of MnBi:Fe thin films," *Journal of Applied Physics* 111 (2012) 07E326.
14. R. Skomski, A. Kashyap, and A. Enders, "Is the magnetic anisotropy proportional to the orbital moment?," *Journal of Applied Physics* 109 (2011) 07E143.
15. R. Skomski, "Are there superspin glasses?," *Journal of Applied Physics* 109 (2011) 07E149.
16. X. Wei, D. Le Roy, R. Skomski, X. Z. Li, Z. Sun, J. E. Shield, M. J. Kramer, and D. J. Sellmyer, "Structure and magnetism of MnAu nanoclusters," *J. Appl. Phys.* 109 (2011) 07B523.
17. B. Balamurugan, R. Skomski, X. Z. Li, V. R. Shah, G. C. Hadjipanayis, J. E. Shield, and D. J. Sellmyer, "Magnetism of cluster-deposited Y-Co nanoparticles," *Journal of Applied Physics* 109 (2011) 07A707.
18. V. Sharma, P. Manchanda, R. Skomski, D. J. Sellmyer, and A. Kashyap, "Anisotropy of heavy transition metal dopants in Co," *Journal of Applied Physics* 109 (2011) 07A727.
19. P. Manchanda, P.K. Sahota, R. Skomski, P.S. Kumar, A. Kashyap, "First-principle description of magnonic Pd_nFe_m multilayers," *Journal of Applied Physics* 109 (2011) 07C110.
20. R. Skomski, B. Balamurugan, T. A. George, M. Chipara, X.-H. Wei, J. E. Shield, and D. J. Sellmyer, "Hysteresis and relaxation in granular permanent magnets," *Journal of Applied Physics* 111 (2012) 07B507.
21. P. K. Sahota, Y. Liu, R. Skomski, P. Manchanda, R. Zhang, H. Fangohr, M. Franchin, G. C. Hadjipanayis, A. Kashyap, and D. J. Sellmyer, "Ultrahard magnetic nanostructures," *Journal of Applied Physics* 111 (2012) 07E345.
22. B. Balamurugan, R. Skomski, X.Z. Li, G.C. Hadjipanayis, D.J. Sellmyer, "Magnetism of directly ordered Sm-Co clusters," *Journal of Applied Physics*, 111 (2012) 07B527.
23. B. Balamurugan, R. Skomski, B. Das, X.Z. Li, V.R. Shah, P. Manchanda, A. Kashyap, D.J. Sellmyer, "Magnetism of dilute Co(Hf) and Co(Pt) nanoclusters," *Journal of Applied Physics* 111 (2012) 07B532.
24. B.Z. Cui, L.Y. Zheng, W.F. Li, J.F. Liu, G.C. Hadjipanayis, "Single-crystal and textured polycrystalline Nd₂Fe₁₄B flakes with a submicron or nanosize thickness," *Acta Materialia* 60 (2012) 1721.
25. B.Z. Cui, L.Y. Zheng, M. Marinescu, J.F. Liu, G.C. Hadjipanayis, "Textured Nd₂Fe₁₄B flakes with enhanced coercivity," *Journal of Applied Physics* 111 (2012) 07A735.
26. L.Y. Zheng, B.Z Cui, W.F Li, G.C. Hadjipanayis, "Separated Sm-Co hard nanoparticles by an optimization of mechano-chemical processes," *Journal of Applied Physics* 111 (2012) 07B536.
27. B. Balamurugan, B. Das, V.R. Shah, R. Skomski, X.Z. Li, D.J. Sellmyer, "Assembly of uniaxially aligned rare-earth free nanomagnets," *Applied Physics Letters* 101 (2012) 122407.
28. B. Balamurugan, D.J. Sellmyer, G.C. Hadjipanayis, and R. Skomski, "Prospects for nanoparticle-based permanent magnets," *Scripta Materialia* 67 (2012) 542.
29. A. Pal, A. Gabay, G.C. Hadjipanayis, "Mechanochemical synthesis of Nd₂Fe₁₄B alloy with high coercivity," *Journal of Alloys and Compounds* 543 (2012) 31.
30. W.F. Li, H. Sepehri-Amin, L.Y. Zheng, B.Z. Cui, A.M. Gabay, K. Hono, W.J. Huang, C. Ni, G.C. Hadjipanayis, "Effect of ball-milling surfactants on the interface chemistry in hot-compacted SmCo₅ magnets," *Acta Materialia* 60 (2012) 6685.

31. C. Chinnasamy, J. Herr, R. Pai, B.Z. Cui, W.F. Li, J.F. Liu, "Gram scale synthesis of high magnetic moment $\text{Fe}_{100-x}\text{Co}_x$ alloy nanoparticles: from synthesis to applications", *Journal of Applied Physics* 111 (2012) 07B539.
32. B.Z. Cui, M. Marinescu, J.F. Liu, "Anisotropic $\text{Nd}_2\text{Fe}_{14}\text{B}$ submicron flakes by non-surfactant-assisted high energy ball milling", *IEEE Transactions on Magnetics* 48 (2012) 2800.
33. O. Akdogan, W. Li, B. Balasubramanian, D.J. Sellmyer, G.C. Hadjipanayis, "Effect of exchange interactions on the coercivity of SmCo_5 nanoparticles made by cluster beam deposition," *Advanced Functional Materials* (2013) 1.
34. W.Y. Zhang, X.Z. Li, S. Valloppilly, R. Skomski, J.E. Shield, D.J. Sellmyer, "Magnetism of rapidly-quenched rhombohedral $\text{Zr}_2\text{Co}_{11}$ -based nanocomposites," *Journal of Physics D: Applied Physics* 46 (2013) 135004.
35. A.M. Belemuk, S.T. Chui, "Temperature-dependent demagnetization behaviour in perpendicular exchange-coupled $\text{SmCo}_5/\text{FeCo}$ multilayers," *Journal of Physics D: Applied Physics* 45 (2012) 125001.
36. A.M. Belemuk, S.T. Chui, "The coercive behavior and the energy product for multilayers of FeCo and Sm-Fe-N ," *Journal of Magnetism and Magnetic Materials* 324 (2012) 3113.
37. A.M. Belemuk, S.T. Chui, "Finite temperature performance of hard-soft composite nanomagnets and its dependence on geometry structure of composites," *Journal of Applied Physics* 113 (2013) 043913.
38. A.M. Gabay, X.C. Hu, G. Hadjipanayis, "Mechanochemical synthesis of fine $\text{R}_2\text{Fe}_{14}\text{BH}_x$ and $\text{R}_2\text{Fe}_{14}\text{B}$ powders with $\text{R} = \text{Nd}$ or Nd-Dy ," *Journal of Alloys and Compounds* 574 (2013) 472-476.
39. I.A. Al-Omari, W.Y. Zhang, L.P. Yue, R. Skomski, J.E. Shield, X.Z. Li, D.J. Sellmyer, "Hf doping effect on hard magnetism of nanocrystalline $\text{Zr}_{18-x}\text{Hf}_x\text{Co}_{82}$ ribbons," *IEEE Transactions on Magnetics*, 49 (2013) 3394.
40. B. Das, B. Balasubramanian, P.K. Sahota, R. Skomski, S. Valloppilly, J.E. Shield, A. Kashyap, D.J. Sellmyer, "HfCo₇-based rare-earth-free permanent-magnet alloys," *IEEE Transactions on Magnetics*, 49 (2013) 3330.
41. B. Das, B. Balamurugan, R. Skomski, X. Z. Li, P. Mukherjee, G. C. Hadjipanayis, D. J. Sellmyer, "Structure and magnetism of dilute $\text{Co}(\text{Zr})$ nanoclusters," *Journal of Applied Physics* 113 (2013) 17B509.
42. W.F. Li, X.C. Hu, B.Z. Cui, J.B. Yang, J.Z. Han, G.C. Hadjipanayis, "Magnetic property and microstructure of single crystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ ultrafine particles ball milled from HDDR powders," *Journal of Magnetism and Magnetic Materials* 339 (2013) 71.
43. W.F. Li, A.M. Gabay, X.C. Hu, C. Ni, G.C. Hadjipanayis, "Fabrication and microstructure evolution of single crystalline $\text{Sm}_2\text{Co}_{17}$ nanoparticles prepared by mechanochemical method," *Journal of Physical Chemistry C* 117 (2013) 10291.
44. R. Skomski, P. Manchanda, P. Kumar, B. Balamurugan, A. Kashyap, D.J. Sellmyer, "Predicting the Future of Permanent-Magnet Materials," *IEEE Transactions on Magnetics* 49 (7) (2013) 3215.
45. R. Skomski, P. Kumar, G.C. Hadjipanayis, D.J. Sellmyer, "Finite-Temperature Micromagnetism," *IEEE Transactions on Magnetics* 49 (2013) 3229.
46. P. Kharel, V.R. Shah, R. Skomski, J.E. Shield, D.J. Sellmyer, "Magnetism of MnBi -Based Nanomaterials," *IEEE Transactions on Magnetics* 49 (2013) 3318.
47. B.G. Kelly, K.M. Unruh, "Preparation and Magnetic Properties of Sub-Micrometer Sized Sm-Co Powders Prepared From Nanostructured Precursor Oxides," *IEEE Transactions on Magnetics* 49 (2013) 3349.

48. W.Y. Zhang, S. Valloppilly, X.Z. Li, Y. Liu, S. Michalski, T.A. George, R. Skomski, J.E. Shield, D. J. Sellmyer, "Magnetism of Rapidly Quenched $\text{Sm}_{1-x}\text{Zr}_x\text{Co}_5$ Nanocrystalline Materials," IEEE Transactions on Magnetism 49 (7) (2013) 3353.
49. A.M. Gabay, W.F. Li, G.C. Hadjipanayis, "Mechanochemical Synthesis of $(\text{Sm},\text{Pr})_2(\text{Co},\text{Fe})_{17}$ Anisotropic Hard Magnetic Powders," IEEE Transactions on Magnetism 49 (2013) 3225.
50. P. Kharel, V.R. Shah, X.Z. Li, W.Y. Zhang, R. Skomski, J.E. Shield, D.J. Sellmyer, "Structural and magnetic properties of Pr-alloyed MnBi nanostructures," Journal of Physics D: Applied Physics 46 (2013) 095003.

B. Papers

N/A

C. Status Reports

Fourteen quarterly reports (Q1 - Q14)

D. Media Reports

1. John Sutter, "The race to make the world's strongest magnet," CNN.com, 03/09/2011
2. (<http://www.cnn.com/2011/TECH/innovation/03/09/rare.earth.magnet.race/index.html>)
3. Tracey Bryant, "Coming attraction," University of Delaware Research, vol. 2, No. 2 (http://www.udel.edu/researchmagazine/issue/vol2_no2_security/coming_attraction.html)
4. G. Hadjipanayis, A. Gabay, "Magnet makeover," IEEE Spectrum 48 (2011) 36-41.
5. Nicola Jones, "Materials science: The pull of stronger magnets," Nature 472 (2011) 22-23.
6. Katie Bourzac, "The Rare-Earth Crisis," Technology Review 114 (2011) 58-63.

E. Invention Disclosures

N/A

F. Patent Applications

N/A

G. Licensed Technologies

N/A

H. Networks/Collaborations Fostered

N/A

I. Websites Featuring Project Work Results

N/A

J. Other Products (e.g. Databases, Physical Collections, Audio/Video, Software, Models, Educational Aids or Curricula, Equipment or Instruments)

N/A

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K. Awards, Prizes, and Recognition

N/A

Follow-On Funding

Additional funding committed or received from other sources (e.g. private investors, government agencies, nonprofits) after effective date of ARPA-E Award.

N/A

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