Progress Report
Jan. 15, 1997- Jan. 15, 2000

United State Department of Energy
GRANT: DE-FG02-97ER45626

for
Continuation of

"Magnetic Properties and Spectroscopic Studies of Selected Rare Earth-Transition Metal Intermetallic Alloys"

Submitted to
Division of Materials Sciences, ER-13
Attn.: Dr. Jerry J. Smith

By
Rama Mohanty
Principal Investigator
Profess of Physics, and Director, Southern Research Institute of Pure and Applied science,

Southern University
Baton Rouge, LA 70813

October, 1999
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
I. Activities

A) Publications


5. "Structural and Magnetic Properties of R$_2Fe_{17-x}Be_x$ compounds where R = Y, Pr, Nd, Sm, Dy and T", Submitted to Journal of Physics, Condensed Matter, R. C. Mohanty, C. Zhang, S. A. Shaheen, A. Raman, and C. G. Grenier


B) Research Activities:

1. Substitutions of elements in NdFe$_5$-equivalent host material were first attempted. These involved mainly partial substitutions of Fe with Co, Cu (or Ga, Al, and Nb) and C. Also some B was added to study the effect of partial substitution of C with B. Compounds of composition Nd$_{16}Fe_{68}Co_xX_2C_9B_{0.5}$, X being Cu, Ga, Al, or Nb. Carbon was introduced mainly to form carbides and about 10 at. % C was already known to dissolve in these compounds. Effect of X element substitution on the hard magnetic properties are to be studied further.
2 Carbon was also introduced into the $\text{Y}_2(\text{Fe, Ga})_{17}$ type compounds to pursue the effects. Up to 10. % C was introduced in $\text{Nd}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}$ host compounds.

3 Substitution of $\text{Fe}$ in $\text{R}_2\text{Fe}_{17}$ compounds by $\text{Be}$ was attempted. Many rare earth elements were chosen for the study. The following series of alloys were made and studied.

\[
\begin{align*}
\text{Pr}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 0, 1, 2, 3 \\
\text{Nd}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 2, 3, 4, 5, 6, 7, 8 \\
\text{Sm}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 0, 1, 2, 3, 4 \text{ and also } \text{Sm}_2\text{Fe}_{17}\text{Be}_{0.2} \\
\text{Gd}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 3, 5, 7 \\
\text{Tb}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 2, 3, 4, 5, 6, 8 \\
\text{Y}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 2, 3, 4, 5, 6, 8 \\
\text{TbY}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 2 \\
\text{Dy}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 2, 3, 4, 5, 6 \\
\text{Er}_2\text{Fe}_{17-x}\text{Be}_x: & \quad x = 1, 3, 5, 7
\end{align*}
\]

There are some reasons to choose these alloys. The first thing, the binary phases of the kind $\text{R}_2\text{Fe}_{17}$ have only the $\text{Th}_2\text{Zn}_{17}$-type structure for the light rare earths (in the case of $\text{Pr}$, $\text{Nd}$, and $\text{Sm}$ among those studied), both $\text{Th}_2\text{Zn}_{17}$ and $\text{Th}_2\text{Ni}_{17}$-types for the middle rare earths up to $\text{Ho}$ and $\text{Y}$ (in our alloys of $\text{Gd}$, $\text{Tb}$ and $\text{Y}$), and only the $\text{Th}_2\text{Ni}_{17}$-type structure for the heavy rare earths beyond $\text{Dy}$ (in our $\text{Dy}$ and $\text{Er}$ alloys). How much $\text{Be}$ dissolves in each of these structures in the various rare earth alloys and whether any one structure is favored by the $\text{Be}$ substitution was studied. Secondly, in substitution by elements $\text{Ga}$, $\text{Al}$, $\text{Si}$ or others, Curie temperature can be increase, but different way for different rare earth. For example, from $\text{R}_2\text{Fe}_{17}$ to $\text{R}_2\text{Fe}_{10}\text{Ga}_7$, Curie temperature decreases for $\text{Gd}$, but increases for $\text{Sm}$, $\text{Tb}$, $\text{Dy}$, $\text{Ho}$, $\text{Er}$, $\text{Tm}$. At last, there is different sign of second-order Stenveins coefficient $\alpha_1$ for different rare earth, and it will affect the anisotropy property very much. So, the overall information can be obtained through those studies.

4 Analysis of the alloys made indicated that in addition to the above mentioned two phases and their solid solutions with $\text{Be}$ another phase with the $\text{NaZn}_{13}$-type cubic structure was also found in these alloys. This prompted the inquiry whether the already known $\text{RBe}_{13}$ phases with the $\text{NaZn}_{13}$-type structure phase found on the Fe-rich side. If such a tie-in were feasible, it would indicate a remarkably large solid solubility of $\text{Fe}$ in the $\text{RBe}_{13}$ compounds. The solubility of $\text{Fe}$ in the $\text{Be}$-rich phases has not been studied extensively so far. Hence the following $\text{Fe}$-substituted $\text{RBe}_{13}$ alloys were also made and evaluated for $\text{Fe}$ solubility in this structure. The alloys made were:

\[
\begin{align*}
\text{RBe}_{12}\text{Fe}, & \quad \text{Where } \text{R} = \text{Pr, Nd, Sm, Tb, Y and Dy} \\
\text{YFe}_{13-x}\text{Be}_x, & \quad x = 5, 6
\end{align*}
\]
LaFe\textsubscript{13-x}Be\textsubscript{x}, x = 3, 4, 6
CeFe\textsubscript{13-x}Be\textsubscript{x}, x = 3, 4, 6
PrFe\textsubscript{13-x}Be\textsubscript{x}, x = 2, 3
NdFe\textsubscript{13-x}Be\textsubscript{x}, x = 2, 3, 4, 5
GdFe\textsubscript{13-x}Be\textsubscript{x}, x = 3, 4, 5
DyFe\textsubscript{4}

After research mentioned above, it is found that there exist the single phase R(Fe,Be)\textsubscript{13} with the NaZn\textsubscript{13}-type structure on the Fe-rich side. This also prompts the inquiry whether other elements can stabilize the RBe\textsubscript{13} phases with the NaZn\textsubscript{13}-type structure. So, the following alloys were also made:

LaFe\textsubscript{13-x}Ga\textsubscript{x}, x = 6, 7
CeFe\textsubscript{13-x}Ga\textsubscript{x}, x = 6, 7
PrFe\textsubscript{Ga}
NdFe\textsubscript{13-x}Ga\textsubscript{x}, x = 6, 7
LaFe\textsubscript{4}Cu\textsubscript{4}
LaFe\textsubscript{4}Ni\textsubscript{4}

LaCo\textsubscript{13} is the only known binary phase with the NaZn\textsubscript{13} structure. When introduced Ga and Si, the ternary Co-alloys with this structure can exist in some light rare earth elements up to Sm. The cubic structure even gets distorted at higher Ga, and Si concentration. So, Be was introduced into RCo\textsubscript{13} to check the effect on the structure and the magnetic properties. The following alloys were studied:

LaCo\textsubscript{13-x}Be\textsubscript{x}, x = 1, 2, 3, 4, 5, 6
NdFe\textsubscript{13-x}Be\textsubscript{x}, x = 2, 3

In addition to the above mentioned series of compounds with the 2:17-type structures, a series of compounds for the ThMn\textsubscript{12}-tape structure were also made studied. The alloys were:

DyCo\textsubscript{10}Mo\textsubscript{2-x}V\textsubscript{x}, where x = 0, 0.5, 1, 1.5, 2 and
DyCo\textsubscript{10}Mo\textsubscript{2-x}V\textsubscript{x}, where x = 0, 0.5, 1, 1.5, 2

The phase present in the samples and the crystal lattice parameters have been determined by X-ray diffraction. The easy magnetization direction of DyCo\textsubscript{10}Mo\textsubscript{2-x}M\textsubscript{x} (M = Si, or V) has been checked by the X-ray diffraction made on powders which were magnetically aligned at room temperature and fixed in the epoxy. SEM was used to observe the microstructure.

Magnetic property characterization of all the alloys made has been started and is progressing.

Main finding from these activities is:
a) The carbon-containing compounds need to be synthesized more carefully by utilizing powder pressing and sintering techniques prior to alloys prepared solely through arc melting showed considerable inhomogeneities.

b) Be substitutes for Fe by different amounts in the different $R_2Fe_{17}$ compounds. Whereas only one Fe atom can be substituted by Be in the Pr alloys, two Fe atoms can be substituted by Be in the case of Nd, and about 4 Fe atom substitution by Be atoms is found to be possible in the case of Sm. The amount of substitution keeps on increasing further in the case of yttrium and heavy rare earth such as Ga, Tb, Dy and Er. All $R_2Fe_{17}$ of these elements dissolve about 5 Be atoms. The lattice parameters linearly decreased with increasing Be concentration, and the decreasing rate is very large, meaning Be atoms occupy the lattice site, not the interstitial site.

c) $R_2Fe_{17}$ with $R = Y$ or the heavy rare earth elements can crystallize with the $Th_2Ni_{17}$-type structure, but substitutional introduction of certain amounts of other elements in the $Th_2Ni_{17}$-type compound can change its structure to $Th_2Zn_{17}$-type. The substitution of Fe by Be in the $R_2Fe_{17}$ compounds stabilizes the $Th_2Zn_{17}$-type structure and promotes the transition from the $Th_2Ni_{17}$-type into the $Th_2Zn_{17}$-type structure more than the substitution by the other elements such as Si, Ga, Al and etc. does. In all cases we studied except for $Er_2Fe_{16}Be$, the Be-substituted $R_2Fe_{17}$ (2:17) phase is crystallized with the rhombohedral $Th_2Zn_{17}$-type structure. $Er_2Fe_{16}Be$ compound shows the $Th_2Zn_{17}$- and the hexagonal $Th_2Ni_{17}$-types. That crystal structure influences the magnetic exchange interaction between Fe atoms, which then affects Curie temperature.

d) For $R_2Fe_{17-x}Be_x$, the saturation magnetic moment drops very fast during the initial substitution. However, the saturation magnetic moment drops slower with more Be substitution. It may mainly come from the electron hybridization. The Curie temperature decreases at a rate that depends on the rare earth element, indicating the Curie temperature is dominated by the magnetic moment, not the exchange interaction between Fe atoms in the case of Be substitution.

e) Calculated using the mean-field theory, the magnetic exchange interaction constant $-J_{Fe-Fe}$ between Fe atoms in $Y_2Fe_{17-x}Be_x$ compound increases sharply at the initial substituted stage followed by a decrease with further substitution. The magnetic exchange interaction constant $-J_{R,Fe}$ between Fe atom and R atom in $R_2Fe_{17-x}Be_x$ compound ($R = Tb$, or Dy) increases monotonously. Those lead to the complex change of the Curie temperature with $x$ in $R_2Fe_{17-x}Be_x$.

f) The Fe-rich NdFe$_{13}$,Be$_x$ (x = 2-4) phase with NaZn$_{13}$ type structure has been prepared by arc melting and subsequent annealing at 1223 K for a
week. The single phase with NaZn$_{13}$ type structure for as-cast alloys with compositions exists at $x$ = 3 and 4. After annealing, the samples with compositions $x$ = 2 and 3 stabilized in the NaZn$_{13}$ type phase with no secondary phases. The NaZn$_{13}$ type phase has a magnetic ordering temperature in excess of 900 K and a small magnetic moment of 0.1-0.2 $\mu_B/(\text{Fe,Nd})$ at 300K. The magnetization at 5K attains a value of 0.8 $\mu_B/(\text{Fe,Nd})$ and saturation is not obtained, thus indicating that magnetic structure may not be simple ferromagnetic. The magnetization decreases with increasing Fe content, which is typical behavior of Invar alloys.

g) For all of the DyCo$_{10}$Mo$_{2-x}$M$_x$ (M = Si or V) alloys, single phase with tetragonal ThMn$_{12}$-type structure can be formed with the co-existing stabilizing elements Mo and V or Si. The lattice constants $a$, and $c$ and the unit cell volume decrease with increasing $x$ in the case of both Si and V, according to Vegard’s law.

h) Although the easy magnetization direction (EMD) of YCo$_{10}$V$_2$ and YCo$_{10}$Si$_2$ is within the basal plane, the EMD of all DyCo$_{10}$Mo$_{2-x}$M$_x$ (M = V or Si) alloys is parallel to the $c$-axis except for the DyCo$_{10}$Si$_2$ alloy which has an EMD within the basal plane. The crystal-field coefficient $A_{20}$ is larger than 0 for all the alloys but for DyCo$_{10}$Si$_2$.

i) For the DyCo$_{10}$Mo$_{2-x}$V$_x$ alloys, there is a spin-reorientation transition from easy $c$-axis to easy cone at a subzero temperature when the temperature is decreasing as the anisotropy contribution due to higher order crystal-field terms gains in importance

j) Huge coercivity at low temperature was also found in these samples. For DyCo$_{10}$Mo$_{1.5}$V$_{0.5}$ alloy, only a minor magnetic hysteresis loop with the coercivity of 4.5 T at 10 K could be measured by the SQUID scanning up to a maximum magnetic field of 5.5 T, and a coercivity of more than 5.5 T has been inferred.

C) Seminars, symposia and communication:

1 In addition to the above activities special seminars were organized regularly and weekly meetings with the students held to train them for research.

2 A one-day symposium on hard magnetic materials was held at Southern University on 7/16/98. A copy of the program carrying the details is attached.

3 Besides cooperation with Louisiana State University, we set up other links with University of New Orleans, Florida State University and others to communicate the academic activities, to use the advanced equipment and to create new research areas.
4 Present two papers in the 44th Annual Conference on Magnetic \& Magnetic Materials, San Jose, California, November 15-18, 1999

II. Activities planned for 2000-03

A) Continue characterization of the alloys already made and development of scientific manuscripts containing research results for publication:

1 Research on magnetic properties of R(Fe,Be)_{13} alloy, especially at high temperature or at high magnetic field, and on the effect of other substituent elements, Ga, Cu, Ni, on the formation of RFe_{13}-type phase and its magnetic properties.

2 Characterize the crystal structure and magnetic properties of R(Co, Be)_{13} alloys.

3 We will continue to research on the coercivity dependence on the grain-size, the 'x' of DyCo_{10}Mo_{2-x}M_x (M = V and Si) and the temperature. Especially high magnetic field measurements will be used to determine how high a coercivity can be attained at different temperatures and to determine the optimum composition for maximum coercivity. At the same time, the effect of x on the coercivity dependence on the temperature will be studied. XRD and TEM or HTEM will evaluate the crystal structure and metallography.

4 Neutron scattering measurement or Mössbauer spectroscopic studies shall be undertaken in order to determine the atom occupation sites in the DyCo_{10}Mo_{2-x}M_x lattice (M = V and Si) for the substitutents Mo, V and Si. The moments of Co-atoms at the different sites in the lattice shall also be probed into.

5 Also determine the preferential occupation site of Be atom and the moments of Fe-atoms at the different site in the R_{2}Fe_{17-}Be_x alloys. The Influence of Be substitution on the magnetic moment and the exchange interaction will be analyzed in detail and deeply.

B) Study on some new alloys and new research areas:

1 Develop new alloys containing Co in the ternary composition of the R_{2}(Fe, Be)_{17}-type. Cobalt is expected to enhance the Curie temperature and the magnetization in these alloys. In addition, introduce other elements like Cu, Zr, C and/or N and evaluate the modifications to properties. The multiple introductions, like R_{2}Fe_{17-x}y_{z}Co_{x}Cu_{y}T_{z}Be_{z} alloys and their carbides or nitrides, will be prepared and characterized.
2 Develop and characterize other 1:12 and 3:29 alloys in the R-Fe-Be or R-Co-Be systems. Modify these compositions with Cu, Zr and others. R(Fe, Co, Be, M)$_{12}$C$_2$ and R$_3$(Fe, Co, Be, M)$_{29}$C$_x$ alloys will also be studied.

3 According to our results on DyCo$_{10}$Mo$_{2-x}$M$_x$ (M = Si, V), other 1:12 alloys of the type RCo$_{12-2y}$M', M' (M' or M'' is another stabilized element), shall be synthesized and characterized to improve the intrinsic magnetic properties.

4 Prepare and investigate RFe$_{13}$xBe$_{6}$, RCo$_{13}$xBe$_{6}$ and RFe$_{13-x-y}$Co$_{x}$M$_y$ alloys, where M = Be, Al, Ti, Ga. At last we will synthesize and characterize RFe$_{13-x-y}$Co$_{x}$M$_y$C$_n$ alloys.

5 The influence of grain-size on the magnetic properties of above alloys with good intrinsic properties will be investigated. Especially the nanocrystalline alloys of them will be prepared and investigated. EXAFS technique will be used to analyze the nanocrystalline powders.

6 Explore novel permanent magnetic materials.

III. Personnel who participated in research:

Faculty:

1. Prof. R.C. Mohanty, P.I.
2. Prof. A. Raman, Co-P.I.
3. Prof. C.G. Grenier, Co-P.I.
4. Pro. R. Ferrell, Scientific Collaborator
5. Dr. C. Zhang, Research Associate
6. Dr. Hong-Shuo Li, External Collaborator from Australia.
7. Dr. S. A. Shaheen, visiting scholar, Florida State University

Graduate students:

1 Mr. Walter Craig, Graduate student at the Ph.D level
2 Mr. Ziab Giadfad, Graduate student at the M.S. level
3 Ms. Iaiaka Akanbi, Graduate student at the M.S. level

Undergraduate students:

1 Ms. Toni Ewing
2 Mr. Jennifer Milleon
3 Ms. Suhaila Ali
4 Ms. Sharon Smith
5 Ms. Wanda M. Azeme
6 Ms. Renite Woods
7 Ms. Marcel Greaves
8 Ms. Carla Blackledge
9 Kimberly D. Gilbert
10 Ms. Genevieve Totesant