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Continuation of

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

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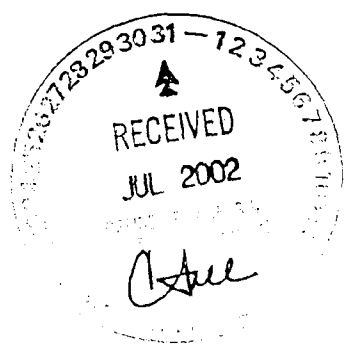

DISCLAIMER

I. Activities

A) Publications

1. "Magnetocrystalline anisotropy of $Y_2Fe_{17-x}Ga_x$, Journal of Magnetism and Magnetic Materials, 166 (1997) 365-373, Hong-Shuo Li, R. C. Mohanty, A. Raman, and C. G. Grenier.
2. "Magnetic Properties of $Nd_2Fe_{14-x}Be_xB$", IEEE transactions on magnetics, Vol. 33, No5 (1997), Hong-Shuo Li, R. C. Mohanty, A. Raman, C. G. Grenier, and J. M. Cadogan.
3. "High Coercivity and Spin Reorientation Transition in $DyCo_{10}Mo_{2-x}V_x$ Compounds", Journal of Magnetism and Magnetic Materials, 1999, in print, C. Zhang, R. C. Mohanty, Hong-Shuo Li, A. Raman, C. G. Grenier, and W. Craig.
4. "Magnetic Properties of $DyCo_{10}Mo_{2-x}Si_x$ Compounds", Journal of Applied Physics, 1999, in print, C. Zhang, R. C. Mohanty, A. Raman, C. G. Grenier, R. E. Ferrel, and S. A. Shaheen.
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,
6. "Effect of Crystal Structure and Exchange Interaction on Curie Temperature in $R_2Fe_{17-x}Be_x$ Compounds", Submitted to Journal of Magnetism and Magnetic Materials, C. Zhang, R.C. Mohanty, A. Raman, C.G. Grenier, and R.E. Ferrell.
7. "Laser Optogolvanic Analysis in a Radiofrequency Plasma: Detection of Iodine Atoms and Molecules", Microchemical Journal 61, 223-239(1999), Xuan Yao, Sean P. McGlynn and Rama C. Mohanty.
8. "Structural and Magnetic Properties of $NdFe_{13-x}Be_x$ compounds", Submitted to the 44th Magnetism and Magnetic Materials conference, San Jose, CA (1999), S. A. Shaheen, C. Zhang, R. C. Mohanty, 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 $Nd_{16}Fe_{68}Co_4X_2C_{9.5}B_{0.5}$, 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. Effected of X element substitution on the hard magnetic properties are to be studied further.

2 Carbon was also introduced into the $Y_2(Fe, Ga)_{17}$ type compounds to pursue the effects. Up to 10. % C was introduced in Nd_2Fe_{17} and Sm_{2Fe17} host compounds.

3 Substitution of Fe in R_2Fe_{17} compounds by Be was attempted. Many rare earth elements were chosen for the study. The following series of alloys were made and studied.

$Pr_2Fe_{17-x}Be_x$: x = 0, 1, 2, 3
$Nd_2Fe_{17-x}Be_x$: x = 1, 2, 3, 4, 5, 6, 7, 8
$Sm_2Fe_{17-x}Be_x$: x = 0, 1, 2, 3, 4 and also $Sm_2Fe_{17}Be_{0.2}$
$Gd_2Fe_{17-x}Be_x$: x = 1, 3, 5, 7
$Tb_2Fe_{17-x}Be_x$: x = 1, 2, 3, 4, 5, 6, 8
$Y_2Fe_{17-x}Be_x$: x = 1, 2, 3, 4, 5, 6, 8
$TbY_2Fe_{17-x}Be_x$: x = 1, 2
$Dy_2Fe_{17-x}Be_x$: x = 1, 2, 3, 4, 5, 6
$Er_2Fe_{17-x}Be_x$: x = 1, 3, 5, 7

There are some reasons to choose these alloys. The first thing, the binary phases of the kind R_2Fe_{17} have only the Th_2Zn_{17}-type structure for the light rare earths (in the case of Pr, Nd, and Sm among those studied), both Th_2Zn_{17} and Th_2Ni_{17}-types for the middle rare earths up to Ho and Y (in our alloys of Gd, Tb and Y), and only the Th_2Ni_{17}-type structure for the heavy rare earths beyond Dy (in our Dy and Er alloys). How much Be dissolves in each of these structures in the various rare earth alloys and whether any one structure is favored by the Be substitution was studied. Secondly, in substitution by elements Ga, Al, Si or others, Curie temperature can be increase, but different way for different rare earth. For example, from R_2Fe_{17} to $R_2Fe_{10}Ga_7$, Curie temperature decreases for Gd, but increases for Sm, Tb, Dy, Ho, Er, Tm. At last, there is different sign of second-order Stenvens coefficient α_J 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 tie above mentioned two phases and their solid solutions with Be another phase with the $NaZn_{13}$-type cubic structure was also found in these alloys. This prompted the inquiry whether the already known RBe_{13} phases with the $NaZn_{13}$-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 Fe in the RBe_{13} compounds. The solubility of Fe in the Be-rich phases has not been studied extensively so far. Hence the following Fe-substituted RBe_{13} alloys were also made and evaluated for Fe solubility in this structure. The alloys made were:

$RBe_{12}Fe$, Where R = Pr, Nd, Sm, Tb, Y and Dy
$YFe_{13-x}Be_x$, x = 5,6

$LaFe_{13-x}Be_x$, x = 3, 4, 6
$CeFe_{13-x}Be_x$, x =3, 4, 6
$PrFe_{13-x}Be_x$, x = 2, 3
$NdFe_{13-x}Be_x$, x = 2, 3, 4, 5
$GdFe_{13-x}Be_x$, x = 3, 4, 5
$DyFe_9Be_4$

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

$LaFe_{13-x}Ga_x$, x = 6, 7
$CeFe_{13-x}Ga_x$, x = 6, 7
$PrFe_7Ga_6$
$NdFe_{13-x}Ga_x$, x = 6, 7
$LaFe_9Cu_4$
$LaFe_9Ni_4$

6 $LaCo_{13}$ is the only known binary phase with the $NaZn_{13}$ 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_{13} to check the effect on the structure and the magnetic properties. The following alloys were studied:

$LaCo_{13-x}Be_x$, x = 1, 2, 3, 4, 5, 6
$NdFe_{13-x}Be_x$, x = 2, 3

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

$DyCo_{10}Mo_{2-x}V_x$, where x = 0, 0.5, 1, 1.5, 2 and
$DyCo_{10}Mo_{2-x}V_x$, 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 $DyCo_{10}Mo_{2-x}M_x$ (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.

8 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 are 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 $-J_{Fe\text{-}Fe}$ 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 $-J_{R\text{-}Fe}$ 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 $NdFe_{13-x}Be_x$ (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 μ_B/(Fe,Nd) at 300K. The magnetization at 5K attains a value of 0.8 μ_B/(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 Möessbauer 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 $R_2Fe_{17-x}Be_x$ 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 $R_2Fe_{17-x-y-r-z}Co_xCu_yT_rBe_z$ 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. $R(Fe, Co, Be, M)_{12}C_z$ and $R_3(Fe, Co, Be, M)_{29}C_{z'}$ 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 $RCo_{12-y}(M', M'')_y$, (M' or M'' is another stabilized element), shall be synthesized and characterized to improve the intrinsic magnetic properties.

4 Prepare and investigate $RFe_{13-x}Be_x$, $RCo_{13-x}Be_x$ and $RFe_{13-x-y}Co_xM_y$ alloys, where M = Be, Al, Ti, Ga. At last we will synthesize and characterize $RFe_{13-x-y}Co_xM_yC_n$ 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 Giadfahd, 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. Jennfer 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