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13. ABSTRACT *(Maximum 200 words)*

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^{57}Fe NMR work on $Fe_{16}N_2$ confirms that the Fe moment is significantly enhanced compared to the moment of elemental Fe. $SmCo_{7-x}Zr_x$ has intrinsic properties which make it deserve attention as a high energy permanent magnet material. $LaCo_{13}$ has large magnetization and high Tc. Unfortunately, it is cubic and hence lacks anisotropy. It can be made uniaxial but then it loses its large Ms and Tc. It has been studied as a soft magnet material in regard to which it shows promise.

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Outline of Report

I. INTRODUCTION

Magnets are ubiquitous in modern society. The average household utilizes in excess of 40 magnets; the average automobile involves more than 20 magnets. Many of these are permanent magnets. These are barium or strontium ferrite magnets, alnico magnets or rare earth-containing magnets. The latter represent a revolutionary development in that they permit magnet energy densities an order of magnitude or more higher than that provided by the alnicos and ferrites. This revolutionary development began with the synthesis of $SmCo_5$(1) but became a marketable item during the 1970s.

In large measure the utility of a permanent magnet is defined by its so-called maximum energy product. The maximum energy product is the maximum value of the product of B and H in the 2nd quadrant of the magnetic hysteresis loop, viz. $(BH)_{max}$. The values for $(BH)_{max}$ are 4 and 6 MGOe for Ba ferrite and alnico 5, respectively. In contrast, a $(BH)_{max}$ value of 52 MGOe has been achieved with the rare earth-containing magnets which are comprised largely of $Nd_2Fe_{14}B$.

The quantity of magnetic material needed for a specific application is inversely related to the energy product of the material used to form the magnet. The major significance of high energy magnetic materials is that they permit significant downsizing of devices. High energy magnets permit downsizing of motors, generators, linear actuators, etc. which is of significance in military and civilian applications. High energy permanent magnets are used not only in electromechanical devices but also in computer peripherals (disk drives), electronic equipment (traveling wave tubes for generating microwaves, etc.)

The highest energy commercial magnets are 45 MGOe magnets, whereas the highest energy laboratory magnets are, as indicated above, 52 MGOe magnets. Very much higher energies are potentially available - up to 350 MGOe for some of the pure elemental rare earths and in excess of 150 MGOe for 3D transition metal alloys and compounds. From present day knowledge of the hysteretic characteristics, the high energy of the elemental rare earths seems to be beyond our reach. However, the high energies of the 3D transition metal systems may be obtainable provided we acquire sufficient understanding of the mechanism of coercivity in such systems.

To obtain a high maximum energy product it is necessary that our magnetic material have a large magnetic induction (B) in the 2nd quadrant of the hysteresis loop. It should be recognized that to retain a large value of the magnetic induction (B) in the 2nd quadrant of the hysteresis loop we are requiring that the material exist in a metastable state. Impurities normally exist in the magnetic material which results in the rapid relaxation of the metastable material to the stable state. Under such circumstances the material has little or no coercive force, is a soft material, has a small value of B in the 2nd quadrant, and has a negligible energy product. If we can arrange matters so as to prevent this rapid relaxation, we have a high coercivity (H_c) and a hard magnetic material. If we simultaneously have a large remanence (B_r), we have a high energy magnet material. Hence, the quest for a high energy magnet material consists in finding a material which has simultaneously a large B_r and a large H_c and at the same time the B-H loop in the second quadrant be nearly linear. To find materials which have a large B_r <u>AND</u> a large H_c is very difficult. Only 5 such materials are known: $SmCo_5$, $PrCo_5$, $Nd_2Fe_{14}B$, $Pr_2Fe_{14}B$, and $Sm_2Fe_{17}N_x$.

The main objective of the work being carried out under ARO contract number DAALO3-91G-0027 has been to find other, hopefully better, high energy magnet materials. The main task is to find a means to generate coercivity. Prospects for this are now brighter than ever because, largely as a consequence of work carried out in recent years at Carnegie Mellon University by the author and his students; major advances have been made toward elucidating the origin of coercivity in high induction (1)*.

II. MILITARY SIGNIFICANCE OF PERMANENT MAGNETS

The significance of magnetic materials has been alluded to in the preceding section, but only briefly. During the Persian Gulf War, it has been reported that several smart devices (missiles, etc.) have been used which utilized permanent magnet compounds of SM_2Co_{17} and $Nd_2Fe_{14}B$. In this section some additional details are given, including some examples of the military utility of high performance magnets. Most military applications can be grouped into two categories: (1) those in which the magnet generates a force influencing the motion of an object of macroscopic dimensions and (2) electronic devices in which a magnet generates a field that affects the motion of a stream of electrons. In the latter category are power devices which generate beams of microwaves - traveling wave tubes, klystrons, gyrotrons - linear induction accelerators, high power free electron lasers, etc. The first category includes all electromechanical force devices - linear actuators, motors, generators, stepper motors, disk drives, voice coil motors, torque couplers, etc.

Often military applications require the highest level of performance. The high energy magnets being developed in the program sponsored by the Army Research Office are directed toward meeting these needs. As an example, $SmCo_5$-Sm_2Co_{17} composites are used in traveling wave tubes (TWT) fabrication. The composites normally used have energy products in the range of 15-18 MGOe. In these materials, which are doped with Fe, Cu, Zr and certain of the heavy rare earths, the energy product falls far short of what is possible and TWT performance suffers accordingly. In the program at Carnegie Mellon University other formulations have been explored, and substantial improvements in the basic magnetic characteristics of the 2:17-type magnets used in TWT fabrication have been made. However, further improvements are possible. This will in turn lead to improved devices for high power microwave generation.

In the permanent magnet field there are two major needs: (1) high energy magnets, which will permit downsizing and even miniaturization of motors, generators and actuators, and (2) cheaper magnets, even ones with modest energy projects - in the range of 10 MGOe. If cost can be sufficiently reduced, magnets in the latter category will supplant ferrites in a wide range of electromechanical devices and will result in improved performance of those devices. There is obvious utility of high energy magnets in that they permit one to fabricate very compact high torque motors and significantly downsized generators.

In a program supported by SDIO and NASA, the Principal Investigator has demonstrated the utility of high energy permanent magnets such as $Pr_2Fe_{14}B$. Several magnets based on $Pr_2Fe_{14}B$ have been synthesized, employing dry processing techniques. Room temperature energy products exceeding 47 MGOe have been found. Brushless-type motors with these magnets have been built which show improved performance characteristics: i.e., a motor constructed with $Pr_2Fe_{14}B$ magnet exhibits nearly 15% greater torque compared to a commercial motor (containing Sm_2Co_{17}-type magnets) of an equivalent size.

In the civilian applications, the current trend appears to be towards the design and development of electric cars. The most acceptable approach appears to be the construction of a hybrid vehicle, where permanent magnets are in critical demand for the design of energy-efficient electric motors and generators. It is generally recognized by the experts that this will be a growth area for the next 10-15 years. Therefore, development of new and more powerful permanent magnets, motors and generators is a highly desirable goal.

The high energy magnets represent a step up the magnetic energy density ladder toward that provided by superconductor electromagnets. The permanent magnets offer the advantage that they perform at room temperature and above. In contrast, superconductor magnets entail liquid helium or nitrogen temperatures. Superconductors operating at room temperature remain at present only a distant dream.

III. PROGRAM OBJECTIVES

There are two major components of the ARO supported program at Carnegie Mellon University. For simplicity these will be referred to as A: The Laboratory Component, and B: The Literature Search Component. All of the A component work has either been reported in the open literature or is currently in press. A brief account of this portion of the work is given below. A full account of this work is given in Appendix A. The reader is referred to the Appendix if he/she is interested in the details of the work.

The strategy employed in seeking useful new magnetic materials is to focus attention on systems rich in Fe and/or Co. For permanent magnets one needs, in addition, high coercivity. Obtaining high coercivity entails, *inter alia*, a large magnetocrystalline anisotropy. The latter is a necessary, but may not be a sufficient, condition.

The A component of the work has led us to focus attention on five systems: $Fe_{16}N_2$, $RCo_{13-x}Si_x$, $RFe_{13-x}Si_x$, $R(Co, Fe)_{13-x}Si_x$, and $SmCo_{7-x}Zr_x$. These will be discussed in turn.

A. The Laboratory Studies

1. $Fe_{16}N_2$ Studies

For some years it has been claimed that Fe in $Fe_{16}N_2$ has an abnormally large magnetic moment - up to 60% larger than that of elemental Fe. This information was based on thin film work. In the preceding contract period M.Q. Huang and W.E. Wallace were able to form bulk quantities of $Fe_{16}N_2$. Unfortunately, the $Fe_{16}N_2$ was formed in a mixture of Fe, γFeN and $Fe_{16}N_2$. These investigators by careful quantitative XRD measurements were able to establish that Fe in $Fe_{16}N_2$ has a significantly enhanced moment but the complexity of the mixture caused some independent investigators to doubt the validity of the Fe moment established in this way.

Discussion of this issue with Professor Joe Budnick of the Physics Department of the University of Connecticut led to a collaborative effort to establish the Fe moment by ^{57}Fe NMR work. This effort confirmed that the Fe in $Fe_{16}N_2$ has an enhanced moment. It also confirmed that the Huang-Wallace XRD determination was correct. It is in the nature of the NMR work that the complexities present in the XRD work of Huang and Wallace are not present in the NMR work.

As noted above, details of this work are given in the two papers in the appendix dealing with $Fe_{16}N_2$.

2. Studies of RCo_{13}-based Systems

$LaCo_{13}$ is the prototype of the RCo_{13}-based systems. It has a large magnetism and high T_c. Hence it possesses two of the required attributes of a high energy magnet material. Unfortunately it is cubic and hence it cannot have either anisotropy or significant coercivity.

Several modifications in composition were instituted in hopes of degrading the cubic symmetry and bringing about tetragonal or hexagonal symmetry:

a. Co in $LaCo_{13}$ was partly replaced by Si to give $LaCo_{13-x}Si_x$;

b. La in $LaCo_{13-x}Si_x$ was replaced by Pr, Nd, Gd or Dy;

c. Composition was adjusted so that the (Co+Si)/R ratio exceeded 13. (We term this the non-stoichiometric system whereas that in (b.) is termed the stoichiometric system.);

d. Inserting nitrogen by treating the alloy with NH_3. (Experiment showed this to have no beneficial effect.)

It was found that the Si doping generated a uniaxial crystal when x=2 but this tetragonal material became a weak magnetic material with T_c in the liquid nitrogen range.

In summary, destroying cubic symmetry and generating non-cubic symmetry by compositional variation was achieved but at the cost of losing the large magnetization and high T_c.

3. Studies of $RFe_{13-x}Si_x$ with R=Pr, Nd and Si

These systems behave in a manner very similar to the corresponding Co systems. However, the T_c values for the Fe systems are somewhat higher than those for the Co systems. Even so the Curie temperatures for the iron systems are below room temperature. Also these alloys do not exhibit a large magnetic moment.

4. $LaCo_{13}$ and $LaCo_{13-x}Fe_x$ as Soft Magnetic Materials

It was shown in the studies just described that the logical compositional variations succeeded in degrading the symmetry of the RCo_{13} alloy but at a calamitous magnetic cost. Magnetism was decreased about 100-fold and T_c was diminished by about 1000°C. Clearly the materials studied lack the potential to be a useful hard magnetic material. In mid-1997 studies of $LaCo_{13}$ were redirected. $LaCo_{13}$ and $La(Fe,Co)_{13}$ alloys began to be studied as soft magnetic materials. They have the potential to qualify as high temperature, high performance soft magnetic materials. These studies indicate that they offer very real promise in this regard. The properties measured, specifically coercivity, were found to be in accord with those expected from structural considerations. $LaCo_{13}$ is indeed soft. Its coercivity is 6 to 9 Oe at room temperature and is even smaller at elevated temperatures. These are the values for bulk samples of $LaCo_{13}$. $LaCo_{0.6}Fe_{0.4}$ behaves in a rather similar way except that its moment is about 15% higher than that of $LaCo_{13}$. Details of this work are given in the appendix. These materials appear to have properties that make them of interest to the DoD.

5. Studies of $SmCo_{7-x}Zr_x$ as a Permanent Magnet Material

Japanese investigators T. Ojima, et al (2) showed a number of years ago that Zr doping improved the properties of 2:17 magnets. Of the many dopants examined the Japanese team found that Zr was the most effective dopant in enhancing the energy products. The reason for the enhancement is yet to be fully clarified. The study of $SmCo_{7-x}Zr_x$ alloys is a step in the direction of clarifying "the Zr effect."

In the study, which is described in detail in the appendix, it has been observed that the anisotropy field (H_A) is increased by about 115% by Zr doping. This is observed at 10K. The improvement is less striking at room temperature but the effect is still impressive.

The cast alloys consist of a complex mixture of rhombohedral (Th_2Zn_{17} type) and hexagonal ($TbCu_7$ type) alloys. The study showed that Zr doping markedly increased the stability of the hexagonal phase. As regards the magnetic behavior, it seems reasonable to presume that "the Zr effect" is at least in part a consequence of the increase of the anisotropy field by Zr doping. This work is being continued and further elucidation of the Zr effect is expected.

B. Literature Search

In 1991 P. Villars and L.D. Calvert under the auspices of the American Society of Metals published a four-volume compendium of Intermediate Phases entitled "Pearson's Handbook of Crystallographic Data for Intermetallic Phases." This compilation contains about 55,000 entries. For each entry composition a minimal amount of structural information was provided. A copy of a page from this compendium is included in the present report to exemplify the information provided.

The Villars-Calvert compendium was screened to select out systems that are (1) uniaxial and (2) rich in Co and/or Fe. About 150 systems have been selected out for extensive study. Alloys are sought which have high T_c's.

In addition, the author is on the editorial boards of *IEEE Trans. Mag.* and the *Journal of Magnetism and Magnetic Material.* Current issues of these journals are carefully examined in search of new materials. These are two of the most prestigious materials in the field of magnetism.

$SmCo_5$, Sm_2Co_{17} and $Nd_2Fe_{14}B$ are the only high energy magnets known at present. Work continues at Carnegie Mellon University to extend this very, very short list. A vigorous effort is underway under the auspices of DARPA. Additional high performance magnetic materials are expected.

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