Studies Involving the Synthesis and Characterization of High Energy Magnet Materials

W. E. Wallace

M. E. Wallace

Carnegie Mellon University
Pittsburgh, PA 15213

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

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Permanent magnets are essential components of a wide range of modern devices, many of which have military significance - travelling wave tubes, klystrons, linear induction accelerators, high power free electron lasers, high performance motors and generators, etc. Higher energy permanent magnets enable one to downsize the various devices which operate via permanent magnets. The present study had as its main objectives: (a) improving existing high energy magnets and (b) developing new magnets. The systems studied with this in mind fall into three structural types: those having (a) the Nd$_2$Fe$_{14}$B structure, (b) the ThMn$_{12}$ structure and (c) the Sm$_2$Co$_{17}$ structure. Results of the studies are presented in 26 papers published in the open literature. Highlights of the work are provided in this report by giving terse summaries of 9 of the papers. The work has been a part of the world-wide effort to make Nd$_2$Fe$_{14}$B magnets into a commercial reality. SmTiFe$_9$Co$_2$ has been established as a promising permanent magnet material. Pr$_2$(Co,Fe)$_{17}$ has also been studied as a promising permanent magnet material and the composition ranges defined that are attractive for magnet fabrication. Magnets fabricated from the alloy of composition Nd$_2$Co$_{0.6}$Fe$_{13.4}$ exhibited an energy product of 7.5 MGOe and an intrinsic coercivity of 8.0 kOe.

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STUDIES INVOLVING THE SYNTHESIS AND CHARACTERIZATION
OF HIGH ENERGY MAGNET MATERIALS

FINAL REPORT

by

W. E. Wallace
Metallurgical Engineering and Materials Science Department
Carnegie Mellon University
Pittsburgh, PA 15213

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ABSTRACT

Permanent magnets are essential components of a wide range of modern devices, many of which have military significance - travelling wave tubes, klystrons, linear induction accelerators, high power free electron lasers, high performance motors and generators, etc. Higher energy permanent magnets enable one to downsize the various devices which operate via permanent magnets. The present study had as its main objectives: (a) improving existing high energy magnets and (b) developing new magnets. The systems studied with this in mind fall into three structural types: those having (a) the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) structure, (b) the \( \text{ThMn}_{12} \) structure and (c) the \( \text{Sm}_2\text{Co}_{17} \) structure. Results of the studies are presented in 26 papers published in the open literature. Highlights of the work are provided in this report by giving terse summaries of 9 of the papers. The work has been a part of the world-wide effort to make \( \text{Nd}_2\text{Fe}_{14}\text{B} \) magnets into a commercial reality. \( \text{SmTiFe}_9\text{Co}_2 \) has been established as a promising permanent magnet material. \( \text{Pr}_2(\text{Co,Fe})_{17} \) has also been studied as a promising permanent magnet material and the composition ranges defined that are attractive for magnet fabrication. Magnets fabricated from the alloy of composition \( \text{Nd}_2\text{Co}_2\text{Fe}_5\text{B}_3 \) exhibited an energy product of 7.5 MGOe and an intrinsic coercivity of 8.0 kOe.
I. INTRODUCTION

This report is concerned with the study of materials needed to fabricate high energy permanent magnets. These are invariably rare earth alloy magnets, which have replaced barium or strontium ferrite magnets or alnico magnets for many applications. The rare earth magnets 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.

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. \((BH)_{\text{max}}\). The values for \((BH)_{\text{max}}\) are 4 and 6 MGOe for Ba ferrite and alnico 5, respectively. In contrast, a \((BH)_{\text{max}}\) value of 52 MGOe has been achieved with the rare earth-containing magnets which are comprised of \(\text{Nd}_2\text{Fe}_{14}\text{B}\).

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 downsizing of devices. High energy magnets permit downsizing of motors, generators, linear actuators, 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 (travelling wave tubes for generating microwaves, etc.).

The highest energy commercial magnets are 35 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. Finding materials with a large B_r is not difficult. To find materials which have a large B_r AND a large H_c is very difficult. Prior to 1985 only one such material was known: SmCo_5. In late 1983 Nd_2Fe_14B was identified as a second high energy magnet material. Its development as an item of commerce has been a worldwide effort.

The main objectives of the work carried out in contract No. DAAL03-87-K-0150 were two-fold: (1) to play a significant role in the worldwide effort to develop Nd_2Fe_14B as a premier permanent magnet material and (2) to find other, hopefully better, high energy magnet materials. The main task was and 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 Dr. J. M. Elbicki, major advances have been made toward elucidating the origin of coercivity in high induction materials. Armed with this knowledge and from the general knowledge developed for magnetic materials, we are now in an improved position to find new and improved magnetic materials. $\text{Pr}_2\text{Fe}_{14}B$ and $\text{SmTiFe}_{11}$ have been particular objects of attention in this regard.

II. MILITARY SIGNIFICANCE OF PERMANENT MAGNETS

The significance of magnetic materials has been alluded to in the preceding section, but only briefly. 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 devices which generate beams of microwaves - travelling wave tubes, klystrons, gyrotrons - linear induction accelerators, high power free electron lasers, etc. The first category includes all electromagnetic 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 present program are directed toward meeting these needs. As an example, $\text{SmCo}_5-\text{Sm}_2\text{Co}_{17}$ composites are used in travelling 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 the foundation is being laid for substantial improvement in the magnets used in TWT fabrication. 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. 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 temperatures. Superconductors operating at room temperature remain at present only a distant dream.

III. RESUME OF MOST RECENT ACCOMPLISHMENTS

A detailed account of new and significant accomplishments in the magnetics program is given in the 26 published papers listed in Table 1. Three of these (Nos. 19-21) are review papers which consolidate and integrate the results of studies of high energy magnets in the program at Carnegie Mellon University
Table 1
Published Papers Emanating from the Program

$R_2Fe_{14}B$ or $R_2Fe_{14}B$-Based Alloys


1:1:11 Systems Forming in the ThMn$_{12}$ Structure


**Hydrides of Strongly Magnetic Rare Earth-Transition Metal Alloys**


14. L. Y. Zhang, F. Pourarian and W. E. Wallace, "Magnetic Behavior of R_2Co_{14} B Hydrides (R = La, Pr, Nd, Sm, Gd, Tb and Y)," *ibid.*, 74, 101 (1988).


**2-17 Systems**


**Reviews**


**Miscellaneous Systems**

and corresponding programs in laboratories throughout the world. Two of the publications (Nos. 17 and 18) deal with the scientifically interesting and industrially important 2:17 systems. We are planning further studies on 2:17 systems and these investigations have helped lay the groundwork for our 2:17 studies planned for the future.

Six studies (Nos. 7-12) are contributions to our understanding of 3, 4 and 5 component systems which occur in the ThMn$_{12}$ structure. Four studies (Nos. 13-16) deal with hydrides of strongly magnetic materials. Six of the studies (Nos. 1-6) involve R$_2$Fe$_{14}$B or R$_2$Co$_{14}$B-based systems. Five studies (Nos. 22-26) deal with a variety of rare earth alloy systems.

Since the papers have all been published in the open literature, a detailed accounting of the work appears unwarranted. Only a few highlights will be cited. Reprints of most of the papers have been sent to ARO. In the cases wherein reprints have not been sent, they will be provided to ARO within the next few weeks.
TV. Some Highlights of Investigations Carried Out

Paper No. 2 *

One of the deficiencies of Nd-Fe-B magnets is their low Curie temperature. The low $T_c$ values for these materials is surprising in view of their large iron content. A similar situation exists in the case of $R_2Fe_{17}$ systems$^3$ where $T_c$ ranges from 468°K (for $Gd_2Fe_{17}$) to 574°K (for $Tb_2Fe_{17}$). Many years ago Givord and Lemaire$^4$ pointed out that in the 2:17 structure the Fe-Fe distances for Fe in the 4f positions (dumbbell sites) are < 2.45 Å and, hence, exchange is negative. They ascribe the low $T_c$ values for the $R_2Fe_{17}$ systems to this effect. It is generally believed that the low $T_c$ values for $Nd_2Fe_{14}B$ arise similarly since many Fe-Fe distances in this material are less than the critical value of 2.45 Å. (There is a range of Fe-Fe distances in this material because its structure involves six Fe sublattices.)

In the study described in paper 2, the result is obtained that replacing Fe with Si results in a sharp increase in $T_c$. Initially, this result is quite surprising in view of the fact that magnetic Fe is being replaced by non-magnetic Si. However, this becomes understandable after it was established that$^5$ Si selectively occupies the Fe($j_1$) and Fe($k_2$) sites. Fe at these sites is that which is primarily responsible for the negative exchange. Once this is appreciated, Si doping is expected to lead to enhancement of $T_c$.

Co doping is usually employed as a means of incrementing $T_c$. It (i.e., Co) has the disadvantage of lowering the coercivity of Nd-Fe-B magnets. Si doping is another way of raising $T_c$. As yet, it has not been established whether this can be done without adversely affecting $H_c$.

Paper No. 5

Another deficiency of $Nd_2Fe_{14}B$ as a permanent magnet material is that it has a change in magnetic structure at $\sim 138°K$. Above this temperature

*The numbers in this section refer to the publications listed in Table I.
this material is uniaxial. Below 138°K the magnetization vector tilts away from the c-axis and lies on the surface of a cone which surrounds the c-axis. The conical configuration does not affect the permanent magnet behavior of Nd-Fe-B magnets at room temperature or above. It does affect the hysteresis behavior at temperatures less than the spin-reorientation temperature, 138°K; it introduces a step in $4\pi M$ VS $H$ curve in the 2nd quadrant of the hysteresis loop. This step has the effect of reducing the maximum energy product at temperatures $<138°K$ as compared with the energy product at room temperature.

This paper shows in detail how the spin-reorientation phenomenon affects hysteretic behavior. It makes clear the fact that Nd-Fe-B magnets are NOT the magnets of choice for use at cryogenic temperatures.

Papers No. 7 and No. 9

Many years ago Kirchmayr \cite{6} discovered a family of intermetallic compounds of the formula $RMn_{12}$. The corresponding Fe compound, i.e., $RFe_{12}$, apparently does not exist. However, several investigators, e.g., Ohashi et al. \cite{7}, have observed that $RV_2Fe_{10}$ and $RTiFe_{11}$ systems exist and they form in the ThMn$_{12}$ structure. The $SmTiFe_{11}$ system is uniaxial (chemical structure tetragonal) with an anisotropy field ($H_A$) of 102 kOe and a saturation induction of 11.6 kG. These features make it of interest as a permanent magnet material, although its $T_c$ of 581°K is somewhat lower than one might like. $T_c$ can be raised by Co-doping, but $H_A$ is simultaneously reduced. The material $SmTiFe_9Co_2$ has the following fundamental properties:

$$B_{sat} = 13.7 \text{ kOe}$$
$$T_c = 729°K$$
$$H_A = 68 \text{ kOe}$$

$$(BH)_{max} = 47 \text{ MGOe (theoretical)}.$$}

These make it attractive as a permanent magnet material. To date, however, no one has succeeded in producing from it a high energy permanent magnet.
In paper 9 it is established that the light rare earths couple ferromagnetically with Fe and the heavy rare earths couple antiferromagnetically with Fe in the RTiFe$_{11}$ systems. Thus, the coupling behavior is the same as that observed for the RFe$_2$, RCo$_5$ and R$_2$Co$_{17}$ systems.

**Paper No. 13**

Hydrogen was introduced into the systems R$_2$Fe$_{14}$B with R = Gd, Tb, Dy, Ho and Er, and the effect of hydrogenation on the bulk magnetic behavior was established. Hydrogenation expands the volume of the lattice by $\sim 3\%$. Magnetization and $T_c$ are found to increase by hydrogenation, whereas $H_A$ is reduced.

Surprisingly, Gd$_2$Fe$_{14}$B hydride exhibits spin reorientation. Upon cooling Gd$_2$Fe$_{14}$BH$_{3.5}$, it transforms from axial to planar at $\sim 325^\circ$K. This kind of transformation has been observed in innumerable systems that have been studied in the ARO program at Carnegie Mellon University. In all cases to date, except the aforementioned hydride, the crystal field interaction involving the rare earth is essential. Competition between the R and transition metal sublattices is the fundamental feature which leads to the aforementioned magnetic transformation. In Gd$_2$Fe$_{14}$BH$_{3.5}$, Gd is in an S-state and hence has essentially negligible crystal field interaction. Thus, in the hydride the spin reorientation must originate with competition between the several Fe sublattices. This phenomenon is both interesting and unique.

**Papers No. 17 and No. 18**

One of the ways to improve Sm-Co 2:17-type magnets is to replace weakly magnetic Sm with strongly magnetic Pr and weakly magnetic Co with strongly magnetic Fe. However, since Pr$_2$Co$_{17}$ is planar, too extensive Pr doping will destroy the uniaxial anisotropy in the (Sm,Pr)$_2$(Co,Fe)$_{17}$ system. The magnetic
phase diagram for $R_2(Co,Fe)_{17}$ with $R = Y, Pr, Sm, Gd, Dy$ and Er has been determined. The composition regions suitable for permanent magnet fabrication have been established. This is essential information for effecting improvements in these systems for use in 2:17-type magnet fabrication.

Papers No. 19, No. 20 and No. 21

These were each invited review papers. No. 19 was presented at the International Symposium on the Properties and Applications of Metal Hydrides V, held at Maubisson, France, May 25-30, 1986. Paper No. 20 was presented at the Materials Research Society Meeting, held in Anaheim, CA, in April, 1987. Paper No. 21 was presented at a symposium arranged by the U.S. Department of Energy and held at Santa Rosa, CA, in November, 1988.

Paper No. 25

This is one of our efforts to discover new, useful magnetic material. This study is concerned with LaCo$_{13}$ and LaCo$_{13}$-based alloys. LaCo$_{13}$ is interesting in many ways. Because of its high Co content it has a large magnetic induction (13 kG) and a high $T_c$ (1318°K) – the largest known $T_c$ for a rare earth system. Unfortunately, LaCo$_{13}$ is cubic and hence is expected to have weak anisotropy and a small coercivity. In this study, LaCo$_{13}$ was doped with Fe and Al. It was of interest to ascertain whether doping would distort this material away from cubic symmetry. This did not occur. However, it was observed that La(Co$_{0.4}$Fe$_{0.6}$)$_{13}$ had a 3d metal moment of 2.39 $\mu_B$ per atom, which is approaching that of 2.46 $\mu_B$/3d atom for Fe$_{0.7}$Co$_{0.3}$. Thus, the La(Co,Fe)$_{13}$ system is a very strongly magnetic material – one of the most strongly magnetic materials known.

Paper No. 26

Another one of our efforts to obtain new, useful magnetic materials is this study of the Nd$_2$(Co,Fe)$_7$B$_3$ quaternary alloy. The structure of this 2:7:3
intermetallic compound is derived from that of the well-known \( \text{RCo}_5 \) compounds. In this there are layers consisting entirely of Co atoms alternating with layers containing both R and Co. Co in the first of these layers is the so-called 3g Co and in the second is the so-called 2c Co. The 2c Co can readily be replaced with B. Various compounds are formed when layers containing the 2c Co and R are replaced by B. This is summarized in Table 2.

<table>
<thead>
<tr>
<th>Fraction of those layers which contain 2c Co and R that have their 2c Co completely replaced by B.</th>
<th>Composition of compound</th>
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<tbody>
<tr>
<td>1/4</td>
<td>( \text{R}_2\text{Co}_9\text{B} )</td>
</tr>
<tr>
<td>1/2</td>
<td>( \text{RCO}_4\text{B} )</td>
</tr>
<tr>
<td>2/3</td>
<td>( \text{R}<em>3\text{Co}</em>{11}\text{B}_4 )</td>
</tr>
<tr>
<td>3/4</td>
<td>( \text{R}_2\text{Co}_2\text{B}_3 )</td>
</tr>
<tr>
<td>1.00</td>
<td>( \text{RCO}_3\text{B}_2 )</td>
</tr>
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</table>

The present study involved the \( \text{Nd}_2\text{Co}_7\text{B} \) system and the quaternary system in which Co is partially replaced by Fe, i.e., \( \text{Nd}_2\text{Co}_{7-x}\text{Fe}_x\text{B}_3 \). \( T_c \) for \( \text{Nd}_2\text{Co}_7\text{B}_3 \) is 330°K, which is so low as to render this material unsuitable for permanent magnet fabrication. However, when doped with Fe its \( T_c \) rises to 716 K. \( \text{Nd}_2\text{Co}_2\text{Fe}_5\text{B}_3 \) was tested for permanent magnet fabrication. Using it, a magnet having induction of 5.9 kG, \( H = 8.0 \text{ kOe} \) and \( (BH)_{\text{max}} = 7.5 \text{ MGOe} \) was obtained. This is a multiphase mixture and by varied analysis the main phase is established as probably being \( \text{Nd}_2(\text{Fe,Co})_{14}\text{B} \).

V. REFERENCES


8. Ref. 3, chapters 10 and 11.