

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

|                                                                                                                                    |                                               |                                                                          |
|------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|--------------------------------------------------------------------------|
| 1. REPORT NUMBER<br>(19) 14517.31-MS                                                                                               | 2. GOVT ACCESSION NO.<br>(18) ARO AD-A084 943 | 3. RECIPIENT'S CATALOG NUMBER<br>(9)                                     |
| 4. TITLE (and Subtitle)<br>(6) Study of Materials Having Significance for High Energy Magnet Production and Hydrogen Storage.      |                                               | 5. DATE OF REPORT PERIOD COVERED<br>Final Report<br>Mar 1977-29 Feb 1980 |
| 7. AUTHOR(s)<br>(10) W. E. Wallace                                                                                                 |                                               | 8. CONTRACT OR GRANT NUMBER(s)<br>(15) ✓ DAAG29-77-G-0110                |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Department of Chemistry<br>University of Pittsburgh<br>Pittsburgh, PA 15260         |                                               | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS              |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>U. S. Army Research Office<br>Post Office Box 12211<br>Research Triangle Park, NC 27709 |                                               | 12. REPORT DATE<br>(11) 15 May 1980                                      |
| 14. MONITORING AGENCY NAME AND ADDRESS (if different from Controlling Office)<br><b>LEVEL II</b>                                   |                                               | 13. NUMBER OF PAGES<br>(12) 23                                           |
|                                                                                                                                    |                                               | 15. SECURITY CLASS. (of this report)<br>Unclassified                     |
|                                                                                                                                    |                                               | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE                               |

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official department of the Army position, policy, or decision unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Permanent magnet materials; rare earth alloys; actinide alloys; hydrogen storage materials; metal hydrides

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A summary is given of work dealing with the development of new permanent magnet materials and new materials for hydrogen storage. The work is reported in detail in 39 publications which have appeared or will appear in the open literature. These include 10 reviews of the subject matter of the program. Among the most significant findings are the following: (1) hydrogen in rare earth and actinide intermetallics behaves as if it were anionic; (2) hydrogenation can either "switch off" or "switch on" ferromagnetism, depending on the system; (3) the superconductor  $\text{Th}_7\text{Fe}_3$  is converted into a ferromagnet when

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(cont. on reverse)

Reproduced From  
Best Available Copy

DDC FILE COPY

DTIC  
ELECTE  
MAY 29 1980

ADA 084313

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

hydrogenated; (4) the mechanism of hydrogen uptake by  $\text{LaNi}_5$  has been thoroughly elucidated; (5)  $\text{Er}_2\text{Co}_{17}$  and  $\text{Yb}_2\text{Co}_{17}$ -based systems have been identified as potentially useful permanent magnet materials; (5) Cr substitution for Co in  $\text{Sm}_2\text{Co}_{17}$  has a powerful beneficial effect on anisotropy.

|                    |                                            |
|--------------------|--------------------------------------------|
| Accession For      |                                            |
| NTIS GRA&I         | <input checked="checked" type="checkbox"/> |
| DDC TAB            | <input type="checkbox"/>                   |
| Unannounced        | <input type="checkbox"/>                   |
| Justification      |                                            |
| By                 |                                            |
| Distribution/      |                                            |
| Availability Codes |                                            |
| Dist               | Avail and/or special                       |
| A                  |                                            |

Reproduced From  
Best Available Copy

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Study of Materials Having Significance  
for High Energy Magnet Production and Hydrogen Storage

by

W. E. Wallace

Final Report

May 15, 1980

to

U.S. ARMY RESEARCH OFFICE

Contract No.: DAAG29-77-G-0110

Period Covered: March 1, 1977 - February 29, 1980

Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA. 15260

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED

Reproduced From  
Best Available Copy

80 5 27 • 280

## Table of Contents

|                                                                             | Page |
|-----------------------------------------------------------------------------|------|
| I. INTRODUCTION . . . . .                                                   | 1    |
| II. REVIEW PAPERS. . . . .                                                  | 1    |
| III. MAGNETISM OF INTERMETALLIC COMPOUNDS . . . . .                         | 2    |
| A. General Comments . . . . .                                               | 2    |
| B. Rare Earth Anisotropy - Single Ion Crystal Field Theory. . . . .         | 3    |
| C. Transition Metal Sublattice Anisotropy . . . . .                         | 4    |
| D. Other Magnetic Studies . . . . .                                         | 7    |
| IV. MAGNETISM OF HYDRIDES OF INTERMETALLIC COMPOUNDS . . . . .              | 7    |
| A. $\text{Th}_7\text{T}_3\text{-H}_2$ Systems . . . . .                     | 8    |
| B. $\text{R}_6\text{Mn}_{23}\text{-H}$ Systems . . . . .                    | 9    |
| C. Sublattice Magnetizations of $\text{RFe}_2\text{-H}_2$ Systems . . . . . | 10   |
| V. FORMATION OF HYDRIDES. . . . .                                           | 11   |
| A. The $\text{LaNi}_5\text{-H}_2$ System. . . . .                           | 11   |
| B. Hydrogen Sorption by Other Systems . . . . .                             | 14   |
| VI. PAPERS PUBLISHED OR IN PRESS . . . . .                                  | 15   |
| A. Review Papers Published. . . . .                                         | 15   |
| B. Magnetism of Intermetallic Compounds . . . . .                           | 15   |
| C. Magnetism of Hydrides of Intermetallic Compounds . . . . .               | 16   |
| D. Formation of Hydrides. . . . .                                           | 17   |
| E. Miscellaneous. . . . .                                                   | 17   |
| BIBLIOGRAPHY . . . . .                                                      | 18   |

## I. INTRODUCTION

The studies carried out under ARO sponsorship fall into two general categories: (1) Magnetization of Intermetallic Compounds and Their Hydrides and (2) Formation of Metallic Hydrides. Studies in these areas carried out in the three-year period extending from March 1, 1977 through February 29, 1980 are described in detail in the 39 publications listed in Section VI below. Since all the significant accomplishments in the work have appeared or will appear in the open literature, the present report is prepared with two objectives in mind: (1) to indicate where the work is published (see Section VI) so that the reader can gain access to it with a minimum of difficulty and (2) to highlight a few of the completed works which appear to be of more than ordinary interest. In Section II a brief account is given of the circumstances which led the author to prepare the 10 review papers listed in Section VI-A. Selected studies pertaining to Magnetism of Intermetallic Compounds, Magnetism of Hydrides of Intermetallic Compounds and Formation of Hydrides are discussed in the subsequent Sections III, IV and V, respectively.

## II. REVIEW PAPERS

The author has been an invited speaker during the current contract period at conferences in Romania, Norway, Germany and India, as well as in the U.S. The review papers involve the contributions at these several conferences and invitations to write chapters in books.

(1)\* was prepared in response to an invitation by Prof. C. Jorgensen of the University of Geneva, Switzerland. The author was an invited speaker at the 23<sup>rd</sup> Annual Conference on Magnetism and Magnetic Materials, held in Minneapolis, MN in November, 1977. (2) is the written version of that lecture. Dr. Barb of the Romanian Institute for Atomic Physics in Bucharest invited the author to address

---

\*Numbers in parentheses refer to the publications listed in Section VI.

the International Conference on Mössbauer Spectroscopy, held in that city in September, 1977. This led to (3).

Prof. G. Alefeld of the University of Munich extended the author an invitation to write a chapter in his book, "Hydrogen in Metals." This is ref. (4). (5) was written in response to an invitation by Prof. K. Strnat, then at the University of California at San Diego, to participate in the Second International Symposium on Coercivity and Anisotropy in Rare Earth-Cobalt Compounds. The Netherlands-Norwegian Reactor School held a Symposium on Metal Hydrides at Geilo, Norway in August, 1977. The author was an invited lecturer (ref. 6).

Prof. E. Wicke of the University of Münster, Germany arranged a Conference on Hydrogen in Metals in Münster in March, 1979. He invited the author to be one of the Plenary Speakers. (7) is the written account of that lecture. This meeting was co-sponsored by the German Bunsengesellschaft and the British Faraday Society.

The author was selected by the Rare Earth Research Conference held in Fargo, ND in July, 1979 to be the first recipient of the Frank H. Spedding Award "for distinguished research in rare earth science and technology." (8) is the Spedding Award address.

(9) is the written version of the invited lecture given at the Symposium on Solid State Chemistry held at Laramie, WY in the summer of 1978. (10) is a copy of the invited lecture given recently in Cochin, India. This was the first Indo-U.S. Conference on the Science and Technology of Rare Earth Materials, held under the joint chairmanship of the author and Prof. E. C. Subbarao of the Institute of Technology in Kanpur, India.

### III. MAGNETISM OF INTERMETALLIC COMPOUNDS

#### A. General Comments

For a material to be of use in the fabrication of high energy permanent magnets (useful in radar equipment, inertial guidance systems and other apparatus

of military significance) it is necessary for it to have a "favorable" crystal field interaction. Since the reason for this is not immediately obvious, a few words of explanation are appropriate.

A permanent magnet is a substance in which the elemental magnets are clamped tightly in place after the alignment field is withdrawn. Granted a high magnetic induction the energy of the magnet, which is related to its utility in devices, directly parallels the strength of the "clamping." In the course of the ARO program of the last decade it has been established that the "clamping" is a consequence of the crystal field interaction. This in turn leads to powerful magnetic anisotropy, i.e., energy of the system which increases rapidly if the magnet moments are rotated away from an energetically preferred direction. The latter is termed the easy direction of magnetization. In short, one of the attributes of a high energy magnet material is a strong uniaxial anisotropy, which derives in turn from the "right" crystal field interaction. To acquire a material with a powerful uniaxial anisotropy it is necessary to understand anisotropy. Since anisotropy derives (largely) from the crystal field interaction in rare earth systems, it was necessary to carry out a number of studies, both theoretical and experimental, to elucidate the crystal field interaction. This has engaged our attention in the ARO program for the last decade or so and has entailed experimental determination of heat capacity, resistivities, as well as magnetic properties.

#### B. Rare Earth Anisotropy - Single Ion Crystal Field Theory

The crystal field interaction is described by a Hamiltonian such as the following:

$$\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 + 2\mu_B \vec{S} \cdot \vec{H}$$

where the B's are crystal field intensity parameters, the O's are Stephens Operators and  $\vec{S}$  and  $\vec{H}$  represent spin of the rare earth ion and applied field,

respectively. From this Hamiltonian one can establish the direction of the easy axis of magnetization and the anisotropy of the rare earth sublattice. (It is to be emphasized that this is only for the rare earth sublattice, not that of the other component - Co, Fe or Ni.) This treatment is termed single ion anisotropy theory. It is described to some extent in the author's monograph, Rare Earth Intermetallics, (Academic Press, Inc., 1973, chapter 3) and in considerable detail in a major review article by W. E. Wallace, S. G. Sankar and V. U. S. Rao, "Crystal Field Effects in Rare Earth Intermetallics" (1). This publication summarizes the formalism developed over the years with ARO support and exemplifies the utilization of this formalism with numerous examples, including the unique high energy magnetic material,  $\text{SmCo}_5$ . The preparation of this review was one of the important accomplishments in the contract period.

There have been two more studies completed dealing with magnetic anisotropy and the crystal field interaction, treated in the context of single ion anisotropy theory (11,38).  $\text{HoAl}_2$  exhibits a heat capacity anomaly at  $\sim 20$  K which originates with a "change in anisotropy," i.e., a change in the direction of the easy axis of magnetization. Analysis of this using a Hamiltonian similar to that above (which is for a hexagonal system, whereas  $\text{HoAl}_2$  is cubic) was made, leading to an evaluation of the various crystal field intensity parameters. Heat capacities of the related compounds  $\text{DyAl}_2$ ,  $\text{ErAl}_2$  and  $\text{LuAl}_2$  were also studied; the Lu compound was included to permit extraction of the non-crystal field heat capacity. Detailed analysis of the data for  $\text{ErAl}_2$  have been made and the crystal field parameters established. This shows inter alia that at temperatures 15 K and lower  $\text{Er}^{3+}$  in this compound exists in the quartet  $\Gamma_8^3$  state and that ferromagnetism develops in this state.

#### C. Transition Metal Sublattice Anisotropy

The above studies have been concerned with the rare earth sublattice contribution to the magnetic anisotropy, i.e., the crystal field interaction. In



$\text{RCo}_5$  systems such as  $\text{SmCo}_5$ , the Co sublattice contributes substantially to the magnetic anisotropy. This contribution, unlike that of the rare earth sublattice, is as yet rather imperfectly understood. A series of studies was undertaken in an effort to clarify the transition sublattice contribution.

The present studies were carried out in the spirit of the investigations of  $\text{YCo}_{5-x}\text{Fe}_x$  and  $\text{ThCo}_{5-x}\text{Fe}_x$  systems studied a number of years ago by Rothwarf, Leupold, Greedan, Wallace and Das [1]<sup>\*</sup> and of  $\text{ThCo}_{5-x}\text{Ni}_x$  by Do Dinh, Narasimhan and Wallace [2]. In these Co systems there are two crystallographically distinguishable types of cobalt - 2c Co and 3g Co. These can be preferentially substituted for by Fe or Ni [3,4], which are less anisotropic than Co. By studying the variation of anisotropy field with composition in carefully selected ternary systems it was established that the 2c Co (which is in the plane with the rare earth) is largely responsible for the Co anisotropy. This was later confirmed by neutron diffraction studies by Desportes et al. [5]. An extension of the Rothwarf et al. study was made by Wallace, Ganapathy and Craig [18] using  $\text{Th}_{1-x}\text{Y}_x\text{Co}_5$  and  $\text{Th}_{1-x}\text{Y}_x\text{Co}_4\text{Fe}$ . This served to corroborate the earlier findings.

Swiss and Japanese workers [6,7] have found that very high energy (>30 MGOe) magnets can be made from  $\text{Sm}_2\text{Co}_{17}$ -based alloys. These are systems in which Co is replaced by Fe, Mn or Cr or some combination of these. The "Rothwarf Effect" is operative here - that is, strengthening of anisotropy by selective replacement of Co with (essentially) isotropic Fe, Mn or Cr. Superficially this seems paradoxical; how can anisotropy be increased by replacing an anisotropic material with an isotropic one? The "Rothwarf Effect" (or perhaps it should be called the "Wallace-Strnat-Rothwarf Effect" since this was observed earlier in several 2-17 systems [8,9]) in these 2:17 systems occurs because of their structural complexity. In the  $\text{RCo}_5$  systems there are, as noted earlier, two kinds of Co.

<sup>\*</sup>The numbers in square brackets refer to the bibliography given on page 1.

In the 2:17 systems there are four kinds of Co. It appears [10,11] that there is only one of the Co varieties which has a favorable anisotropy - the Co in planes with the rare earths. The others are deleterious. These can be preferentially replaced by Fe, Mn or Cr, suppressing their deleterious effect. Thus  $\text{Sm}_2\text{Co}_{17-x}\text{T}_x$  where T = Fe, Mn or Cr or some combination of these, is a better permanent magnet material than  $\text{Sm}_2\text{Co}_{17}$ . Several studies of  $\text{Sm}_2\text{Co}_{17}$ -based systems have been carried out to elucidate further the Wallace - Strnat-Rothwarf Effect. Merches, Sankar and Wallace (14) studied  $\text{Sm}_2\text{Co}_{17-x}\text{Ni}_x$  and  $\text{Y}_2\text{Co}_{17-x}\text{Ni}_x$ . The progression of properties noted was in keeping with the general understanding of this kind of ternary alloy.

In a very thorough study of 2:17 systems of potential interest as high energy permanent magnets Narasimhan and Wallace examined (12) the following systems:  $\text{Yb}_2\text{Co}_{17-x}\text{Fe}_x$ ,  $\text{Er}_2\text{Co}_{17-x}\text{T}_x$  (T = Fe, Mn, Ni),  $\text{Nd}_2\text{Co}_{17-x}\text{Al}_x$  and  $\text{Sm}_2\text{Co}_{17-x}\text{Al}_x$ .  $\text{Er}_2\text{Co}_{17}$ - and  $\text{Yb}_2\text{Co}_{17}$ -based ternaries were identified in this study as potentially useful permanent magnet materials. Merches, Narasimhan and Wallace enlarged (15) on the earlier study by showing that the quaternary systems  $(\text{Er},\text{Pr})_2(\text{Co},\text{Fe})_{17}$  and  $(\text{Er},\text{Pr})_2(\text{Co},\text{Mn})_{17}$  are even more attractive than the systems which did not contain Pr. The argument is rather complex and the Ph.D. thesis of M. Merches (University of Pittsburgh, 1978) should be consulted for full details. The essence is as follows: (1) Pr couples ferromagnetically with Co whereas Er (or Yb) couples antiferromagnetically. Hence replacement of Er or Yb by Pr raises the magnetization; (2) Pr substitutes preferentially for Er in such a way as to enhance anisotropy. Evidence for this preferential substitution is provided by Er Mössbauer spectroscopy [12]. Additional 2:17 studies by Satyanarayana, Wallace and Craig (19) involved work on  $\text{Er}_2\text{Co}_{17-x}\text{T}_x$  and  $\text{Sm}_2\text{Co}_{17-x}\text{T}_x$  where T = Ni or Cr. This work showed that Cr has a remarkable effect in increasing the anisotropy field.

As noted in Section II the writer was invited to speak on recent developments in understanding anisotropy in rare earth intermetallics at the Second International Symposium on Anisotropy and Coercivity of Rare Earth Permanent

Magnet Materials held at the University of California at San Diego in July, 1978. His paper (5) pointed out that anisotropy, while imperfectly understood, is still well enough understood that it can be beneficially manipulated by intelligent alloying.

The preceding sentence is a very terse abbreviation of an argument which would require many pages to present in detail. The argument is reasonably well set forth in the written version of the author's talk at the Anisotropy-Coercivity Symposium alluded to above. That article, which incorporates and expands upon the ideas briefly summarized in the four preceding paragraphs, provides a rather up-to-date assessment of where we stand in the understanding of magnetic anisotropy in the technologically important rare earth alloys. Two other studies relating to anisotropy have been completed (13,18). Results obtained in these works are of interest and significance but in the interest of brevity they are not described in detail here.

#### D. Other Magnetic Studies

Two other magnetic studies warrant comment. Rivillo and Wallace (21) synthesized and studied the ternary systems  $R_{1-x}Ca_xAl_2$  where  $R = Pr$  or  $Gd$ . The objective was to ascertain whether coupling could be reversed, as expected from the RKKY coupling mechanism, by replacing trivalent  $R$  with divalent  $Ca$  and thereby altering the electron concentration. There was suggestive evidence brought forth in this investigation that this does occur. Malik, Wallace and Vijayaraghavan (17) studied the effect of varying crystal fields on the magnetic behavior of  $Sm^{3+}$  ions. It is found that for certain values of the crystal field parameters the  $Sm^{3+}$  ion behaves like an L+S rather than an L-S ion. In this case Sm-Co coupling would be antiferromagnetic. This may be the situation in  $SmCo_5$ .

#### IV. MAGNETISM OF HYDRIDES OF INTERMETALLIC COMPOUNDS

Studies of the magnetism of hydrogenated metals are useful in elucidating the electronic nature of these materials. This is, in turn, helpful in the

understanding of factors contributing to hydride formation. A better appreciation of these factors greatly facilitates the search for new hydrogen storage materials.

The work on hydrogenated intermetallics is described in detail in the eleven publications listed below in Section VI-C. In this section only a few highlights will be presented. The work to be described pertains to the hydrides of (1)  $\text{Th}_7\text{T}_3$ , where  $\text{T} = \text{Fe}, \text{Co}$  and  $\text{Ni}$ , and (2)  $\text{R}_6\text{Mn}_{23}$  systems, where  $\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$  or  $\text{Er}$ .

#### A. $\text{Th}_7\text{T}_3\text{-H}_2$ Systems

$\text{Th}_7\text{T}_3$  systems ( $\text{T} = \text{Fe}, \text{Co}$  or  $\text{Ni}$ ) hydrogenate to compositions  $\text{Th}_7\text{T}_3\text{H}_x$  with  $x \approx 25$ . Thus about 75% of the atoms in the system are hydrogen. The host metals are superconductors with transition temperatures near 2 K. When  $\text{Th}_7\text{Fe}_3$  is hydrogenated to  $\text{Th}_7\text{Fe}_3\text{H}_{30}$ , it becomes a superconductor with an estimated Curie temperature of 350 to 400 K [13]. This appears to be the only instance in which a superconductor has been transformed into a ferromagnet by hydrogenation. In some respects this is roughly the converse of the effect of hydrogenation on Pd. Elemental Pd is an exchange-enhanced paramagnet. When hydrogenated (or deuterated), it becomes a superconductor [14].

The behavior of  $\text{Th}_7\text{Fe}_3$  and its hydride suggest that when the intermetallic is formed, electrons are transferred from Th to Fe to fill the Fe 3d band. The absence of a local moment enables superconductivity to develop in  $\text{Th}_7\text{Fe}_3$ . When the material is hydrogenated, H and Fe are in competition for the electrons supplied by Th. Hydrogen in the rare earths is essentially anionic and it seems likely that it will behave as an anion in  $\text{Th}_7\text{Fe}_3\text{H}_{30}$ . If so, it undoubtedly acquires its electron at the expense of the high energy electrons in the d-band of Fe. Thus conditions are ripe for the development of a local moment in Fe, with the consequent destruction of superconductivity and the possibility of

developing magnetic order. The behavior of hydrogenated  $\text{Th}_7\text{Fe}_3$  is in keeping with the observed behavior of several rare earth-iron compounds to the effect that hydrogenation often [15,16] (2) [but not invariably (24)] increases the moment of Fe in the compound.

Results obtained in a recent Mössbauer study of  $\text{Th}_7\text{Fe}_3\text{H}_{14.2}$  are consistent with the ideas set forth in the preceding paragraph. Viccaro et al. (26) find for this hydride at 300 K only a quadrupole interaction, rather similar to that observed for the host metal, indicating that this material is not magnetically ordered at 300 K. Evidently, with the lower hydrogen content the Fe d-band in  $\text{Th}_7\text{Fe}_3$  either remains fully populated after hydrogenation or it is insufficiently depopulated to lead to a cooperative magnetic state at 300 K.

The corresponding Ni and Co systems were examined to ascertain whether they, too, become ferromagnetic when hydrogenated (29). They do not. Evidently the d-band is too full in this case to permit ferromagnetism to develop.

These studies make it clear that hydrogen captures electrons from the host metal and suggest that the  $\text{Th}^{4+}\text{-H}^-$  interaction is the important factor in the stability of these materials.

#### B. $\text{R}_6\text{Mn}_{23}\text{-H}$ Systems

Several research studies were completed involving metal-hydrogen systems (22,30,32). Research coming from only two of these will be mentioned since the objective of this report is merely to highlight the most significant findings.  $\text{Th}_6\text{Mn}_{23}$  and  $\text{Y}_6\text{Mn}_{23}$  are isostructural and each absorbs hydrogen copiously, ~30 atoms of H per formula unit. The Th compound is a Pauli paramagnet whereas  $\text{Y}_6\text{Mn}_{23}$  is a ferromagnet (Curie temperature ~ 400 K). Upon hydrogenation the roles are reversed, i.e.,  $\text{Y}_6\text{Mn}_{23}\text{H}_{30}$  is a Pauli paramagnet whereas  $\text{Th}_6\text{Mn}_{23}\text{H}_{30}$  is a ferromagnet. This suggests that H absorbs electrons in  $\text{Th}_6\text{Mn}_{23}$  to make this hydride the electronic equivalent of  $\text{Y}_6\text{Mn}_{23}$ . This observation reinforces

the tentative conclusion reached in the previously described studies of  $\text{Th}_7\text{T}_3\text{-H}_2$  systems that hydrogen acts as an electron absorber in these systems.

Since  $\text{Y}_6\text{Mn}_{23}$  loses its ferromagnetism when hydrogenated, it is clear that the local moment on Mn is destroyed during hydrogenation. Inasmuch as Y is non-magnetic, this material is thereby converted to a Pauli paramagnet during hydriding. It was not clear what would happen in a corresponding system  $\text{R}_6\text{Mn}_{23}$  when R is magnetic. Several such systems have been studied, with  $\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$  and  $\text{Er}$ , and unusual magnetic features have emerged. Exchange is weakened in these systems. For example, Curie temperatures for  $\text{Gd}_6\text{Mn}_{23}$  and its hydride are 468 and  $\sim 150$  K, respectively. In this series magnetic ordering is observed only for hydrides of  $\text{Gd}_6\text{Mn}_{23}$  and  $\text{Tb}_6\text{Mn}_{23}$ . The corresponding hydrides with  $\text{R} = \text{Dy}, \text{Ho}$  and  $\text{Er}$  behave in an anomalous fashion. They are probably spin glasses at low temperatures.

#### C. Sublattice Magnetizations of $\text{RFe}_2\text{-H}_2$ Systems

The bulk magnetic characteristics of hydrides of rare earth-iron systems are discussed at length in the author's review article, "Magnetism of Hydrogenated Intermetallic Compounds Containing d-Transition Metals" (7). Neutron scattering work has been carried on in collaboration with Dr. J. J. Rhyne of the National Bureau of Standards involving several  $\text{RFe}_2$  hydrides (24) [17,18]. It is found that the Fe sublattice magnetization is either enhanced or maintained during hydrogenation of the  $\text{RFe}_2$  systems. However, the Fe-Fe exchange is weakened. Work by Malik and Wallace (23) on  $\text{GdNi}_2$  hydride showed that the Gd-Gd exchange is weakened by hydrogenation. Therefore it appears that the entry of hydrogen into the lattice weakens both the R-R and T-T exchange.

$\text{ErFe}_2\text{H}_{3.5}$  displays (24) a rather remarkable feature, one so rare that it may be unique. The Er sublattice disorders rapidly with rising temperature and is paramagnetic for  $T > 300$  K. The Fe sublattice in this hydride disorders

more slowly with increase of temperature and becomes entirely disordered at 450 K. Thus the Er and Fe sublattices have DIFFERENT Curie temperatures.

## V. FORMATION OF HYDRIDES

$\text{LaNi}_5$  is the paradigm hydrogen host material. It is well-known to form rapidly and reversibly the hydride  $\text{LaNi}_5\text{H}_6$ . The formation of this hydride was examined in very considerable detail during the present contract period. Elucidation of the mechanism of hydride formation in this particular system is clearly an important step in elucidating the hydride formation mechanism in general. This analysis is set forth in detail in a publication by the author, Karlicki and Imamura (36).

### A. The $\text{LaNi}_5\text{-H}_2$ System

Since hydrogen is absorbed dissociatively into  $\text{LaNi}_5$ , it is clear that a sequence of events of considerable complexity is involved in the sorption process. Obviously dissociation of  $\text{H}_2$  at the surface is involved, but it had not been clear whether this is rate determining for absorption. More generally, the factors responsible for the rapid absorption or release of hydrogen have not to date been adequately revealed. Desorption by the  $\text{LaNi}_5$ , several  $\text{R}_2\text{Co}_7$  systems ( $\text{R}$  = a rare earth),  $\text{DyFe}_3$  and  $\text{ErFe}_3$  has been found to be [19] second order with respect to the concentration of hydrogen in the hydride. This suggested that recombination of hydrogen atoms at the surface was rate controlling. However, desorption of hydrogen from hydrided  $\text{RFe}_2$  systems studied by Imamura and Wallace [20] obeyed first order kinetics. Additionally, Soga, Ikeda and Imamura [21] have studied  $\text{H}_2/\text{D}_2$  isotopic exchange over  $\text{LaNi}_5$  and find it to be several orders of magnitude more rapid than the uptake or release of hydrogen. This seems to indicate that recombination is not rate controlling. With the improved knowledge of the surface features which has recently been acquired, these seemingly contradictory facts can be resolved.

The absorption process can be described in terms of the following five steps:

- (1)  $H_2(g) \rightarrow H_2(ads.)$
- (2)  $H_2(ads.) \rightarrow 2H(ads.)$
- (3) diffusion along the interface between Ni and  $La_2O_3$
- (4) diffusion in  $LaNi_5$
- (5)  $\alpha$  to  $\beta$  phase transformation.

Surface studies have shown [22-24] that the surface of  $LaNi_5$  is oxidized to form  $La_2O_3$  and Ni to a depth of 50 to 100 Å. Since  $La_2O_3$  and Ni are impervious to hydrogen, entry to the underlying  $LaNi_5$  is gained by diffusion of H along the Ni- $La_2O_3$  interface (step 3 above). Results of Soga et al. in regard to  $H_2/D_2$  exchange [21] exclude the possibility that steps (1) or (2) are rate determining. Steps (4) and (5) are excluded by another kind of measurement made by Soga, Imamura and Ikeda [25]. They flowed  $C_2H_4$  over hydrogenated  $LaNi_5$  and were able to remove hydrogen by the reaction of  $C_2H_4$  to form  $C_2H_6$ . The rate of the process could be established by measuring the rate of  $C_2H_6$  formation. This is found to be about two orders of magnitude faster than the rate of desorption produced by reducing the ambient hydrogen pressure. Clearly neither diffusion in  $LaNi_5$  nor the rate of the  $\alpha/\beta$  phase transformation can be rate determining.

The picture which then emerges is as follows: (a)  $H_2$ , which is chemisorbed on the metallic Ni in the surface, is rapidly dissociated into atoms. (b) monatomic hydrogen is transferred into the interfacial region. (c) Once in the interfacial region it rapidly migrates to the underlying  $LaNi_5$ . H in this interfacial region is very mobile because it is partially bonded to O in the  $La_2O_3$  grain on one side and to Ni on the other. (d) After reaching the underlying  $LaNi_5$  it quickly enters and penetrates and in time gives rise to the  $\beta$  phase. These can be related to the five steps above: Step 2 - (a); Step 3 - (c); Steps (4) and (5) - (d). The author believes that (b) is rate determining.



that is, the rate of transfer of monatomic hydrogen from the Ni grains to the interfacial region. Molecular hydrogen can chemisorb in this region, adopting a configuration  $O\text{---}H\text{---}Ni$ , blocking the passage of H. Here O is a part of the  $La_2O_3$  grain and Ni is part of the Ni grain.

Entry of H into the intergranular region is controlled by the rate of decomposition of the blocking  $H_2$  units. Some of these are stable and will form a complete barrier against hydrogen entry. Others, where the O-Ni spacing is different and unfavorable will be unstable. The rate of entry of  $H_2$  will be controlled by the decomposition rate of these unstable units. The number of these units will be proportioned to the applied pressure of  $H_2$ . Hence,

(1) Rate  $\propto P$ , where P is the applied hydrogen pressure.

If hydrogen is absorbed from a fixed volume container, equation (1) becomes

$$(2) \frac{dP}{dt} = -k_1 P, \text{ or}$$

(3)  $P_0 - P = k_1 P_0 t$  for small times ( $P_0$  is the initial pressure).

Equation (3) agrees with experiment for absorption as determined by Boser [26]. Boser's results indicate for desorption that  $\frac{1}{P_f - P} \propto t$ , where  $P_f$  is the final pressure achieved when hydrogen desorbs into a closed container. This is equivalent to

$$(4) \frac{1}{C_H} = k_2 t + \text{constant}, \text{ where } C_H \text{ is the concentration in the hydride.}$$

Equation (4) indicates that desorption is second order and implies recombination of atomic hydrogen as rate determining. It appears that formation of  $O\text{---}H\text{---}Ni$  by 2 H atoms at the top of the interfacial region is rate determining. H-H, so formed, readily desorbs.

Soga et al. find that hydrogen extraction with  $C_2H_4$  leads, as noted above, to much faster kinetics and to a process 1<sup>st</sup> order with respect to H. It has been pointed out elsewhere (36) that this implies  $C_2H_4$  chemisorption at the

blocking sites instead of  $H_2$  and a rate controlled by intergranular diffusion. This will be the case when the reaction is very fast.

#### B. Hydrogen Sorption by Other Systems

Desorption of  $H_2$  from  $Dy_2Co_7$ ,  $DyCo_3$ ,  $DyFe_3$  and  $ErFe_3$  showed [19] 2<sup>nd</sup> order kinetics. The similarity of these results and the fact that  $RCo_5$  systems show surface oxidation effects similar to those of  $LaNi_5$  suggested that the mechanism proposed for  $LaNi_5$  is quite general. There is no reason to believe that it does not apply to the aforementioned Co and Fe compounds. However, it appears not to apply to  $RFe_2$  systems since, as noted earlier, in this case desorption is second order [20].

The  $RFe_2$  systems ( $R = Gd, Tb, Ho, Er, Tm$ ) release hydrogen much more rapidly than  $LaNi_5$ . They behave as the latter material when dehydrogenated by  $C_2H_4$  and hence 1<sup>st</sup> order kinetics comes as no surprise. However, the  $RFe_2$  systems have three phases [26] (10): Fe, Fe oxide and  $R_2O_3$  in the surface and hence three interfaces. Therefore desorption through the surface layers is a more complex phenomenon with these systems than with  $LaNi_5$ . Moreover, it has been established that the oxide formation at the surface is thinner on the  $RFe_2$  systems than on  $LaNi_5$ . This, too, is involved in the altered kinetic features.

## VI. PAPERS PUBLISHED OR IN PRESS

## A. Review Papers Published

1. W. E. Wallace, S. G. Sankar and V. U. S. Rao, "Crystal Field Effects in Rare Earth Intermetallic Compounds," Structure and Bonding, Vol. 33, Springer-Verlag (1977), p. 1.
2. W. E. Wallace, S. K. Malik, T. Takeshita, S. G. Sankar and D. M. Gualtieri, "Magnetic Properties of Hydrides of the Rare Earths and Rare Earth Intermetallics," J. Appl. Phys. 49, 1486 (1978).
3. W. E. Wallace, "Hydrogenation of Rare Earth Elements and Rare Earth Alloys in Relation to Their Magnetic and Electrical Properties," Proc. Int. Conf. on Mössbauer Spectroscopy, Bucharest, Romania, D. Barb and D. Tarina, eds., Vol. 2 (1978), p. 163.
4. W. E. Wallace, "Magnetic Properties of Metal Hydrides and Hydrogenated Intermetallic Compounds," in Topics in Applied Physics, Vol. 28: Hydrogen in Metals, I, Basic Properties, G. Alefeld and J. Völkl, ed. Springer-Verlag (1978), p. 169.
5. W. E. Wallace, V. U. S. Rao, S. G. Sankar and M. Merches, "Magnetic Anisotropies of Ternary Rare Earth Alloy Systems," Proc. of the Second Int. Sympos. on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys, K. Strnat, ed. Available from the School of Engineering, University of Dayton (1978), p. 118.
6. W. E. Wallace, "Magnetic and Electrical Properties of Rare Earth and Rare Earth Intermetallic Hydrides," in Hydrides for Energy Storage, A. F. Andresen and A. J. Maeland, eds., Pergamon Press, Inc. (1978), p. 33.
7. W. E. Wallace, "Magnetism of Hydrogenated and Intermetallic Compounds Containing d-Transition Metals," Z. f. Phys. Chem., 115, 395 (1979).
8. W. E. Wallace, "Studies of Rare Earth Intermetallic Compounds and Rare Earth Hydrides," The Spedding Award Address, 14<sup>th</sup> Rare Earth Research Conf. Proc., accepted.
9. W. E. Wallace, R. S. Craig and V. U. S. Rao, "Hydrogen Absorption by Intermetallic Compounds," Advances in Chemistry, to appear, April, 1980.
10. W. E. Wallace, A. Elattar, H. Imamura, R. S. Craig and A. G. Moldovan, "Intermetallic Compounds: Surface Chemistry, Hydrogen Absorption and Heterogeneous Catalysis," in The Science and Technology of Rare Earth Materials, W. E. Wallace and E. C. Subbarao, eds., Academic Press, Inc., New York, accepted.

## B. Magnetism of Intermetallic Compounds

11. S. G. Sankar, S. K. Malik, V. U. S. Rao and W. E. Wallace, "Effects of Magnetic Anisotropy on the Heat Capacity of  $\text{HoAl}_2$ ," in Crystal Field Effects in Metals and Alloys, A. Furrer, ed., Plenum Press, New York (1977), p. 153.

12. K. S. V. L. Narasimhan and W. E. Wallace, "Magnetic Anisotropy of Substituted  $R_2Co_{17}$  Compounds ( $R = Nd, Sm, Er$  and  $Tb$ )," IEEE Trans. Mag. MAG-13, 1333 (1977).
13. A. G. Moldovan, S. K. Malik and W. E. Wallace, "Structural and Magnetization Studies on  $ThCo_{5-x}Mn_x$  and  $ThNi_{5-x}Mn_x$  Ternaries," phys. stat. sol.(a), 43, 34 (1977).
14. M. Merches, S. G. Sankar and W. E. Wallace, "Effect of Substitution of Nickel on the Magnetic Properties of  $Sm_2Co_{17}$ ," J. Appl. Phys. 49, 2055 (1978).
15. M. Merches, K. S. V. L. Narasimhan and W. E. Wallace, "Effect of Rare Earth and Transition Metal Substitutions on the Anisotropy of  $R_2Co_{17}$  Compounds," in The Rare Earths in Science and Technology, G. J. McCarthy and J. J. Rhyne, Plenum Press, NY (1978), p. 409.
16. S. K. Malik, T. Takeshita and W. E. Wallace, "Magnetic Behavior of  $RCu_4Al$  ( $R = Gd, Tb, Dy$  and  $Ho$ ) Compounds," ibid., p. 429 (1978).
17. S. K. Malik, W. E. Wallace and R. Vijayaraghavan, "Crystal-Field Effects on the Crossover Temperature of  $Sm^{3+}$  Magnetization in Magnetically Ordered Samarium Compounds," Phys. Rev. B 19, 1671 (1979).
18. W. E. Wallace, E. V. Ganapathy and R. S. Craig, "Magnetism of  $ThCo_5$ -based Alloys," J. Appl. Phys. 50(3), 2327 (1979).
19. M. V. Satyanarayana, W. E. Wallace and R. S. Craig, "Effects of Substitution of Chromium and Nickel on the Magnetic Properties of  $Er_2Co_{17}$  and  $Sm_2Co_{17}$ ," ibid., 2324 (1979).
20. S. K. Malik, W. E. Wallace and T. Takeshita, "Magnetic Behavior of  $RCu_4Al$  ( $R =$  a Rare Earth) Intermetallic Compounds II," 14<sup>th</sup> Rare Earth Research Conf. Proc., accepted.
21. T. Rivillo and W. E. Wallace, "Magnetism and Phase Relations of the  $PrAl_2$ - $CaAl_2$ ,  $GdAl_2$ - $CaAl_2$  Systems," J. Sol. State Chem., accepted.

#### C. Magnetism of Hydrides of Intermetallic Compounds

22. S. K. Malik, T. Takeshita and W. E. Wallace, "Hydrogen Induced Magnetic Ordering in  $Th_6Mn_{23}$ ," Solid State Commun. 23, 599 (1977).
23. S. K. Malik and W. E. Wallace, "Hydrogen Absorption and Its Effect on Structure and Magnetic Behavior of  $GdNi_2$ ," Sol. State Commun. 24, 283 and 417 (1977).
24. J. J. Rhyne, S. G. Sankar and W. E. Wallace, "Sublattice Magnetization of  $ErFe_2-H$ ," in The Rare Earths in Science and Technology, G. J. McCarthy and J. J. Rhyne, eds. Plenum Press, NY (1978), p. 63.
25. S. G. Sankar, D. M. Gualtieri and W. E. Wallace, "Low Temperature Magnetic Properties of the Hydrides and Deuterides of  $Er(Fe_{1-x}Mn_x)_2$ ," ibid., p. 69, (1978).

26. P. J. Viccaro, G. K. Shenoy, B. D. Dunlap, D. G. Westlake, S. K. Malik and W. E. Wallace, "<sup>57</sup>Fe Mössbauer and Magnetization Study of Th<sub>7</sub>Fe<sub>3</sub> and the Hydride Th<sub>7</sub>Fe<sub>3</sub>H<sub>n</sub>," J. de Physique, coll C5, Suppl. No. 5, 40, C2-157 (1979).
27. W. E. Wallace, "Magnetism of Hydrogenated Rare Earth Intermetallic Compounds," 14<sup>th</sup> Rare Earth Research Conf. Proc., accepted.
28. S. K. Malik, E. B. Boltich and W. E. Wallace, "Effect of Hydrogen Absorption-Desorption on the magnetic Susceptibility of CeNi<sub>4</sub>Al," J. Sol. State Chem., submitted.
29. S. K. Malik, E. B. Boltich and W. E. Wallace, "Effect of Absorbed Hydrogen on Magnetic Behavior of Th<sub>7</sub>Co<sub>3</sub> and Th<sub>7</sub>Ni<sub>3</sub>," Solid State Commun., accepted.
30. F. Pourarian, E. B. Boltich, W. E. Wallace and S. K. Malik, "Effect of Absorbed Hydrogen on Magnetic Ordering in Tb<sub>6</sub>Mn<sub>23</sub> and Dy<sub>6</sub>Mn<sub>23</sub>," J. Less-Common Metals, submitted.
31. E. B. Boltich, S. K. Malik and W. E. Wallace, "Magnetic Behavior of the Hydrides of Th<sub>7</sub>Fe<sub>3</sub>, Th<sub>7</sub>Co<sub>3</sub> and Th<sub>7</sub>Ni<sub>3</sub>," *ibid.*, submitted.
32. F. Pourarian, E. B. Boltich, W. E. Wallace, R. S. Craig and S. K. Malik, "Magnetic Characteristics of R<sub>6</sub>Mn<sub>23</sub> Hydrides (R = Gd, Ho and Er)," J. Magnetism and Magnetic Materials, accepted.

#### D. Formation of Hydrides

33. T. Takeshita and W. E. Wallace, "Hydrogen Absorption in Th(Ni,Al)<sub>5</sub> Ternaries," J. Less-Common Metals 55, 61 (1977).
34. D. M. Gualtieri and W. E. Wallace, "Hydrogen Capacity and Crystallography of ErFe<sub>2</sub>-based Ternary Systems," *ibid.*, 55, 53 (1977).
35. T. Takeshita, S. K. Malik and W. E. Wallace, "Hydrogen Absorption in RNi<sub>4</sub>Al (R = Rare Earth) Ternary Compounds," J. Sol. State Chem. 23, 271 (1978).
36. W. E. Wallace, R. F. Karliceck, Jr. and H. Imamura, "On the Mechanism of Hydrogen Absorption by LaNi<sub>5</sub>," J. Phys. Chem. 83, 1708 (1979).
37. W. E. Wallace, R. F. Karliceck, Jr. and H. Imamura, "On the Kinetics of Hydrogen Absorption by Rare Earth Intermetallics," 14<sup>th</sup> Rare Earth Research Conf. Proc., accepted.

#### E. Miscellaneous

38. T. Inoue, S. G. Sankar, R. S. Craig, W. E. Wallace and K. A. Gschneidner, Jr., "Low Temperature Heat Capacities and Thermal Properties of DyAl<sub>2</sub>, ErAl<sub>2</sub> and LuAl<sub>2</sub>," J. Phys. Chem. Solids 38, 487 (1977).
39. T. Takeshita, S. K. Malik and W. E. Wallace, "Crystal Structure of RCu<sub>3</sub>Ag and RCu<sub>4</sub>Al (R = Rare Earth) Intermetallic Compounds," J. Sol. State Chem., 23, 225 (1978).

## BIBLIOGRAPHY

1. F. R. Rothwarf, H. A. Laupold, J. Greedan, W. E. Wallace and D. K. Das, *Int. J. of Magnetism* 4, 267 (1973).
2. K. S. V. L. Narasimhan, C. Do-Dinh, W. E. Wallace and R. D. Hutchens, *J. Appl. Phys.* 46, 4961 (1975).
3. M. Atoji, I. Atoji, Do Dinh Chieu and W. E. Wallace, *J. Appl. Phys.* 44, 5096 (1973).
4. J. Laforest and J. S. Shah, *IEEE Trans. Mag.* MAG-9, 217 (1973).
5. J. Déportes, D. Givord, J. Schweizer and F. Tasset, *ibid.*, MAG-12, 1000 (1976).
6. Proceedings of the Third International Workshop on Rare Earth-Cobalt Permanent Magnets, K. J. Strnat, editor, LaJolla, CA (1978).
7. Proceedings of the Fourth International Workshop on Rare Earth Permanent Magnets, K. J. Strnat, editor, Hakone, Japan (1979).
8. H. J. Schaller, R. S. Craig and W. E. Wallace, *J. Appl. Phys.* 43, 3161 (1972).
9. A. E. Ray and K. J. Strnat, *IEEE Trans. Mag.* MAG-8, 516 (1972).
10. K. Inomata, *Jap. J. Appl. Phys.* 15, 821 (1976).
11. K. Inomata, unpublished report in the Toshiba Co., Kawasaki, Japan, entitled "Spin Orientation in R-Co Intermetallic Compounds." Transmitted by Dr. Inomata as a private communication to the author.
12. M. Merches, Ph.D. Thesis, University of Pittsburgh, 1978, to be published.
13. S. K. Malik, T. Takeshita and W. E. Wallace, *Sol. State Commun.* 28, 359 (1978).
14. T. Skoskiewicz, *Phys. Stat. Sol.(a)* 11, K123 (1972).
15. D. M. Gualtieri, K. S. V. L. Narasimhan and W. E. Wallace, *AIP Conf. Proc.* 34, 219 (1976).
16. S. K. Malik, T. Takeshita and W. E. Wallace, *Mag. Lett.* 1, 33 (1976).
17. J. J. Rhyne, G. E. Fish, S. G. Sankar and W. E. Wallace, *J. de Physique*, coll C5 Suppl. No. 5, 40, C5-209 (1979).
18. G. E. Fish, J. J. Rhyne, S. G. Sankar and W. E. Wallace, 14<sup>th</sup> Rare Earth Res. Conf. Proc., accepted.
19. A. Goudy, W. E. Wallace, R. S. Craig and T. Takeshita, *Advances in Chem. Series* 167, 312 (1978).
20. H. Imamura and W. E. Wallace, *Proc. 14<sup>th</sup>* Rare Earth Res. Conf., accepted.

21. K. Soga, H. Imamura and S. Ikeda, Nippon Kagaku Kaishi 9, 1304 (1977).
22. H. C. Siegmann, L. Schlapbach and C. R. Brundle, Phys. Rev. Lett. 40, 972 (1978).
23. A. G. Moldovan, Ph.D. Thesis, University of Pittsburgh (1978).
24. Th. von Waldkirch and P. Zürcher, Appl. Phys. Lett. 33, 689 (1978).
25. K. Soga, H. Imamura and S. Ikeda, J. Phys. Chem. 81, 1762 (1977).
26. O. Boser, J. Less-Common Metals 46, 91 (1976).
27. A. G. Moldovan and W. E. Wallace, unpublished measurements.