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

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A considerable part of the work has been concerned with "the Zr Effect," the
beneficiation of permanent magnet properties of rare earth-cobalt systems by doping with small amounts (w 1 wt%) of Zr (or Ti or Hf). It has been found that Zr replaces Co in R2Co17 systems, and this results in a sharp increase in magneto-crystalline anisotropy. This is responsible for part (but undoubtedly not all) of the Zr effect.

Systems such as ErPrCo17 are found to exhibit enhanced magneto-crystalline anisotropy, compared to Er3Co17 or Pr3Co17, since Er and Pr are observed to preferentially occupy the 2b and 2d sites, respectively. In these sites each has uniaxial anisotropy, as predicted from single ion anisotropy theory. Preferential site occupancy occurs because of the size difference between Er and Pr. Similar effects are observed in RPrCo17 systems with R = Tm or Yb. Co in CePd3 is in a mixed valent state. Si can be introduced in the lattice to form CePd3SiX. This ternary contains Ce in the Ce3+ state.

Studies of RCo2-xFeX hydrides show that whereas the R and Co moments are decreased by hydrogenation, the Fe moment is unchanged. In Y6Re23 the Fe moment is actually raised about 30% by hydrogenation, to 2.6 μB. The results suggest that H removes electrons from the Fe d-band.

The work to date indicates that surface features are highly significant for materials involved in hydrogen storage and for those materials involved in the fabrication of high energy magnets. It appears likely that surface Co is the nucleation site for inverse domains and may hence control coercive force.
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by

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I. INTRODUCTION

The work for the period July 1, 1980 to June 30, 1983 falls into two general categories: (1) Study of the Magnetic Properties of Intermetallic Compounds and (2) The Study of Metallic Hydrides. The completed work is described in detail in the 44 publications listed in Section VI below. Since all the significant accomplishments in the work have appeared 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 6 review papers listed in Section VI-A. Selected studies pertaining to Magnetism of Intermetallic Compounds, Magnetism of Hydrides of Intermetallic Compounds and Surface Chemistry as it relates to magnetism and hydride formation are discussed in the subsequent Sections III, IV and V, respectively.

II. REVIEW PAPERS

It seems appropriate to indicate the circumstances which led to the six review papers given in Section VI below. The author was selected as the recipient of the first Frank H. Spedding Award for excellence in Rare Earth research. (1)* was the Spedding Award Address. (2) was an invited address at a conference on Solid State Chemistry. (3) and (8) formed part of the first binational U.S.-India Conference on Rare Earth Materials, held in Cochin, India.

*The numbers in parenthesis refer to the publications listed in Section VI.
in 1980. The author was Chief-of-Party of a contingent of 10 Americans who
took part in that conference. (4) was an invited lecture which was presented
at the 14th Rare Earth Research Conference. A NATO Advanced Study Institute
was held in Rhodes, Greece in 1980. (5) is the written version of two invited
lectures given at that Institute.

Collectively, these reviews provide summary accounts of (1) the magnetism
of the industrially important $R_2Co_{17}$ systems, (2) the mechanism of hydride
formation in hydrogen storage materials and (3) the effects of hydrogenation
on the electronic properties of metallic systems, revealed primarily by magnetic
measurements.

III. MAGNETISM OF INTERMETALLIC COMPOUNDS

A. Rare Earth Systems - Enhancing Anisotropy

1. The Zr Effect

It is well known that additions of small amounts of Zr (\(\sim 1\text{ wt\%}\)) has a
remarkable effect in improving the practical magnetic properties - energy pro-
ducts and coercive forces - of $Sm_2Co_{17}$-based alloys. This is also the case
for Ti and Hf additions. For simplicity, this influence of Zr, Ti or Hf doping
on permanent magnet properties is called "The Zr Effect." The origin of this
effect is at present obscure. It has been partially elucidated in publications
numbers 16, 17, 19 and 26 in Section VI.

A necessary, but not sufficient, condition for a large energy product is
a strong magnetocrystalline anisotropy. $SmCo_5$ is exceptional in this respect.
Its anisotropy field ($H_A$) is roughly 400 kOe. In contrast, $Sm_2Co_{17}$ exhibits an
$H_A$ of about 50 kOe, which is small for practical applications. One possibility
for the occurrence of the Zr Effect is that Zr enters the lattice and sharply
increases $H_A$. The several studies mentioned in the preceding paragraph were
initiated to examine this possibility.
Earlier work* had shown that $H_A$ is increased in $R_2Co_{17}$ systems by the substitution of Co in these materials by Fe, Mn, Cr, etc. It seemed possible, therefore, that Zr, etc., would have a similar but larger effect. Therefore $R_2Co_{17}$ systems (with $R =$ Ce, Sm, Er and Yb) were doped with V, Ti, Zr and Hf and their magnetic properties examined. Initially it was not clear where these elements would substitute – for $R$ or for Co. A variety of evidence indicated that Zr, etc., substituted for Co. The strongest evidence was crystallographic in nature. The unit cell increased in size with increasing doping. This is expected if Zr replaces Co because of the relative sizes involved. If $R$ were replaced by Zr, a smaller atom, a shrinkage in unit cell size would be anticipated.

Actually, there was an even earlier question: Would Ti, Zr, etc., enter the $R_2Co_{17}$ lattice? It was not clear at the outset of this work that this would occur. Perhaps they would separate out entirely. Again, crystallographic evidence provided decisive information. For example, it was found that whereas $Sm_2Co_{17}$ has the rhombohedral $Th_2Zn_{17}$ structure, $Sm_2Co_{16}Zr$ has the hexagonal $Th_2Ni_{17}$ structure. This structure change clearly indicates that Zr is entering the lattice.

Experiment showed that Zr is 2 to 3 times more effective in enhancing $H_A$ than Fe, Mn or Cr. The substituent effect in $R_2Co_{17-x}T_x$ alloys is in the order $T = Zr > V > Hf > Ti > Cr > Mn > Fe > Cu$. It thus appears that a part, but probably not all, of the Zr Effect is the strengthening of the magnetocrystalline anisotropy of the system. Presumably this occurs because Zr preferentially substitutes at the Co dumbbell sites, removing the adverse effect of this

kind of Co on $H_A$. This, at present, is merely a postulate which needs to be subjected to experimental test.

2. Increasing $H_A$ by Rare Earth Substitution

In a material such as $\text{Er}_2\text{Co}_{17}$ (hexagonal, $\text{Th}_2\text{Ni}_{17}$ structure) there are two crystallographically distinguishable types of rare earth. In Wyckoff notation these are atoms (or ions) in the 2b and 2d sites. Single ion anisotropy theory shows that the interaction is always opposite at these two sites. If $R$ at the 2b site exhibits uniaxial anisotropy, then $R$ at the 2d site exhibits planar anisotropy; and vice versa. If one could form a system $R'R''\text{Co}_{17}$ in which $R'$ and $R''$ occupied the 2b and 2d sites preferentially, and if these rare earths were chosen so that the interactions in both cases were uniaxial, then $H_A$ would be substantially increased over that for $R'_2\text{Co}_{17}$ or $R''_2\text{Co}_{17}$. This follows because in the binary systems there is always competition between the rare earths in the 2b and 2d sites, and this competition keeps $H_A$ artificially low.

$\text{ErPrCo}_{17}$ is a favorable system if Er and Pr occupy the 2b and 2d sites, respectively. $^{166}\text{Er}$ Mössbauer spectroscopy indicates (14) that the desired site occupancy does (partly) occur. Replacement of 20% of Er by Pr in $\text{Er}_2\text{Co}_{17}$ leads to a 40% increase in the room temperature value of $H_A$ (paper 14 in Section VI). Similar effects were observed in $\text{Tm}_2\text{Co}_{17}$- and $\text{Yb}_2\text{Co}_{17}$-based systems. These systems are discussed in papers (8),(12),(20) and (26) in the list in Section VI.

B. Systems Exhibiting Miscellaneous Effects

In paper (22) it is shown that a valence change for Ce in $\text{CePd}_3$ can be induced by introducing Si to form the ternary alloy $\text{CePd}_3\text{Si}_x$, where $0 \leq x \leq 0.3$. Ce in $\text{CePd}_3$ is in a mixed valence state, as indicated by its crystallographic features and also by its susceptibility. With Si introduction, both of these
measurements indicate a transformation into Ce$^{3+}$. Expansion of the lattice by Si entry enlarges the space available for Ce in the lattice and favors the formation of the larger tripositive ion.

Co forms many Laves phase compounds. These can be represented as ACo$_2$. The ACo$_2$ systems are exchange-enhanced Pauli paramagnets if A is non-magnetic, e.g., YCo$_2$, and are ferromagnetic (or ferrimagnetic) if A is magnetic, e.g., PrCo$_2$. ZrCo$_2$ is a paramagnetic material. It was found (11) that ZrCo$_2$ can be made hyperstoichiometric in Co, and this non-stoichiometric material becomes ferromagnetic at low temperatures. Magnetic ordering occurs only for ZrCo$_x$ where $x \geq 2.8$. Curie temperatures reach 160$^\circ$K in this system.

Th$_6$Mn$_{23}$ and Y$_6$Mn$_{23}$ are isostructural. They are face-centered cubic materials with 116 atoms per unit cell. Th$_6$Mn$_{23}$ is a Pauli paramagnet; Y$_6$Mn$_{23}$ is a ferrimagnet with $T_c = 480^\circ$K. The ordered magnetism in Y$_6$Mn$_{23}$ is quenched by hydrogenation, whereas hydrogenation induces magnetic order in Th$_6$Mn$_{23}$. Given these contrasting features, it was of interest to ascertain the behavior of Th$_6$-Y$_x$Mn$_{23}$ ternary alloys. These ternaries exist in the Th$_6$Mn$_{23}$ structure for all values of x, from 0 to 6.

The ternaries are found to be magnetically ordered for $1.5 \leq x \leq 6$. $T_c$ steadily increases as the Y content of the ternary alloys is increased. Th$_3$YMn$_{23}$ exhibits only short-range magnetic order.

IV. HYDROGENATION AND ITS EFFECT ON MAGNETISM

In studies of RCo$_2$-xFe$_x$ hydrides (37) it was found that hydrogenation simultaneously decreases $T_c$, the cobalt moment and the R-Co and R-Fe exchange interactions. In contrast, there is little change in the iron moment by hydrogenation. The effect of hydrogenation on iron moments in rare earth-iron systems is further alluded to below, where an actual increase in Fe moment is observed.
In studies (34) of ZrMn$_2$ and its hydrides it has been observed that ZrMn$_2$ is a Pauli paramagnet ($x = 1.6 \times 10^{-3}$ emu/formula unit at 295°K), whereas ZrMn$_2$H$_{3.6}$ is a weak ferromagnet with $T_c = 143°K$. The work seems to show that hydrogen extracts electrons from the d-band. This and the enlargement of the lattice transforms the host metal from a Pauli paramagnet into an ordered magnetic material.

Rare earth intermetallics of the formula R$_6$Fe$_{23}$ are of considerable interest. At one time it was thought that they, being predominantly Fe alloys, would be economical hydrogen host materials. It now appears that the hydrides they form are too stable to be used for hydrogen storage. Even so, they are very interesting scientifically and they have been thoroughly examined in this laboratory. Interest has centered on the location of hydrogen and the influence of hydrogen on magnetic behavior.

In (33) it was found that (cubic) Er$_6$Fe$_{23}$ becomes tetragonal when hydrogenated to Er$_6$Fe$_{23}$H$_{14}$. When further enriched in hydrogen, the material becomes cubic again.* Examination of these material by neutron diffraction (42) indicates why these crystallographic changes occur. There are three equivalent sets of sites in planes perpendicular to x, y and z axes. At $\frac{H}{\text{Er}_6\text{Fe}_{23}} = 14$ two of these sets of sites are occupied by hydrogen, whereas one set is empty. This asymmetry leads to the tetragonal distortion.* When further hydrogenated, the other set of sites is populated and cubic symmetry is restored.

In studies of Y$_6$Fe$_{23}$ and its hydride, it was observed** that the magnetization (in $\mu_B$/f.u.) of Y$_6$Fe$_{23}$ and Y$_6$Fe$_{23}$H$_{16}$ are 45.4 and 59.8, respectively. This indicates Fe moments of 2.0 and 2.6 $\mu_B$/atom in the parent alloy and

hydride, respectively. The reduced moment in the parent alloy, compared to elemental Fe, is ascribed to electron transfer from Y to Fe, resulting in a more nearly filled d-band. Similar reasoning suggests that H removes electrons from the d-band during hydrogenation. The large Fe moment is one of the largest, if not the largest, Fe moment observed in metallic systems.

V. SURFACE CHEMISTRY, MAGNETISM AND HYDRIDE FORMATION

The model developed several years ago for the hydrogenation of LaNi$_5$ is as follows:

1. LaNi$_5$ oxidizes to give La$_2$O$_3$ + Ni at the surface.
2. H$_2$ adsorbs dissociatively on the surface Ni.
3. Monatomic hydrogen penetrates the oxidized surface layers and reaches the underlying bulk.
4. Diffusion of H in LaNi$_5$ occurs.
5. As the H content builds up, the rhombohedral $\beta$ phase forms.
6. Step 3 is rate-controlling.

The presence of elemental d-transition metal is essential for rapid hydrogenation kinetics.

Similar surface features undoubtedly exist for RCo$_5$ and R$_2$Co$_{17}$ systems which are significant as permanent magnet materials. Undoubtedly, R$_2$O$_3$ and Co exist in the surface. Co is magnetically soft and may be the site for nucleation of inverse domains. The surface cobalt may control coercivity. It in turn is generated by oxidation.

From these remarks, it is clear that the surface chemistry provides a conceptual link between studies of hydrogen storage materials and high energy

magnet materials. Surface oxidation is deleterious in the second case but not in the first. The present studies focus attention on the importance of establishing surface chemistry in the development of new, technologically significant magnetic materials.
VI. PAPERS PUBLISHED

A. Review Papers Published


B. Magnetism of Intermetallic Compounds


*This is also a review paper.


C. Magnetism of Hydrides of Intermetallic Compounds


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