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Magnetic and Structural Properties of $Y_{6-x}Er_xFe_{23}$ Alloys and Their Hydrides*

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The magnetic characteristics and structural features of the $Y_{6-x}Er_xFe_{23}$ alloys and their hydrides are reported. The parent alloys all formed in a face-centered cubic structure. A pronounced minimum in the lattice parameter was observed for $Er_4Y_2Fe_{23}$. A similar minimum was also observed in the 1 atm hydrogen capacity of the alloys. The hydrides of the Y-rich compounds were found to retain the cubic structure of the parent compounds, whereas the hydrides of Er_5YFe_{23} and Er_6Fe_{23} adopt tetragonally distorted structures. Both the intermetallics and their hydrides were observed to be ferrimagnetic, exchange-dominated systems. In all cases, absorption of hydrogen resulted in an increase in both the saturation magnetization and the Curie temperature.

Introduction

Rare earth–transition metal (*R–T*) compounds of the 6:23 stoichiometry, and more recently their hydrides, have been the subject of a great deal of experimental study, both in this laboratory and elsewhere. The heavy rare earths form 6:23 compounds with both Mn and Fe (*1*). The Fe compounds are much more difficult to prepare and hence they have been the subject of far less study than their Mn analogs. Both the Mn and Fe compounds absorb significant amounts of hydrogen under ambient conditions, the Mn absorbing approximately 23 H atoms per formula unit and the Fe compounds approximately 16 H atoms per formula unit (*2–4*).

The 6:23 compounds crystallize in the Th_6Mn_{23} structure (space group *Fm*3*m*) with 116 atoms per unit cell (*5*). The transition metal atoms occupy four distinct crystallographic sites (b, d, f_1, f_2) and the rare earth atoms occupy the e site. Two of the Fe compounds, Y_6Fe_{23} and Ho_6Fe_{23}, have been studied by neutron diffraction (*6. 7*). These studies indicate that all the Fe moments are coupled ferromagnetically to each other and (in the case of Ho_6Fe_{23}, at least) antiferromagnetically to the rare earth. It is to be noted that this coupling scheme does not carry over into the Mn compounds (*8*).

It has been observed in previous investigations that both Er_6Fe_{23} and its hydride are ferrimagnetic (*9, 10*). It has also been observed that upon hydrogenation, Er_6Fe_{23} transforms from a cubic to a tetragonal crystal structure (*10*).

In a previous study (*4*) the magnetic and

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structural features of $Y_{6-x}Gd_xFe_{23}$ and their hydrides were studied. That study indicated that hydrogenation markedly increased the magnetic moment of Fe to, for example, 2.6 μ_B/Fe atom in the case of $Y_6Fe_{23}H_{16}$. The present work was undertaken (1) to ascertain whether there is a comparable effect, i.e., an increase in Fe moment, in another related system; $Y_{6-x}Er_xFe_{23}$ was chosen for study. It was also of interest to determine (2) whether the Er moment is substantially quenched from the free ion value (as in the Mn compounds) and (3) whether the magnetization of the hydride is sensitive to the structure of the crystal.

The method of this investigation is similar to that employed in the earlier study (*4*). By substituting Er for Y in Y_6Fe_{23} one should be able to draw a fairly strong conclusion regarding the magnitude of the Er moment. It should be noted that the method used here to determine the Er moment, i.e., study of the change in magnetization with incremental variations in composition, is more reliable than merely comparing the magnetization of the end members. Since the end members differ significantly from each other in at least one physical property (the crystal structure of their hydrides), it is inappropriate to assume a priori that they possess the same Fe moment. In regard to the third objective of the study, it is accessible by preparing the hydrides of the pseudobinary compounds and noting whether the magnetization varies continuously or discontinuously with composition between the cubic and tetragonal hydrides.

Experimental

The parent materials were prepared by r.f. induction melting of stoichiometric amounts of the constituent metals in a water-cooled copper boat, under a purified argon atmosphere. The samples were turned and remelted several times to ensure homogeneity. Prolonged annealing at 1100°C was required to obtain single-phase materials. The length of the heat treatment varied from 3 hr for Y_6Fe_{23} to 4 days for Er_6Fe_{23}. The quality of the samples were verified by both X-ray diffraction and high temperature thermomagnetic analysis.

The hydrides studied were those stable at 1 atm with respect to desorption. The hydrides were prepared according to the following procedure. A sample of approximately 2 g was polished with a rotary grinder to remove surface oxide. The sample was then weighed, placed in a system of known volume, and heated to ~200°C under constant pumping for 12 hr. The sample was permitted to cool and then exposed to a known amount of high purity hydrogen at a pressure of ~45 atm. It should be noted that unlike the Mn compounds, some of the samples required a short heating period to attain equilibrium within a 1-day period. Once equilibrium was attained the excess hydrogen was removed by bubbling through water into an inverted buret. SO_2 was then admitted to the system to poison the surface of the hydride, according to the method of Gualtieri *et al.* (*11*). The hydride was then transferred, in a glove bag containing 1 atm of hydrogen, to the sample holder used for the low temperature magnetic measurements.

All X-ray measurements were made on a Diano XRD 700 diffractometer equipped with a graphite diffracted beam monochromator. The radiation employed was Cu K_α, and all diffraction patterns were recorded for 2θ values ranging from ~20 to ~65°.

Magnetic measurements were made on loose powders using the Faraday technique. The temperature dependence of the magnetization was measured in an applied field of 20 kOe between 4.2 and 273 K. The field dependence of the magnetization was measured at 4.2 K. Two types of magnetization versus applied field curves were obtained by the following procedure. The sample was cooled at 4.2 K with no field present; the magnetic field was then applied gradually and initial magnetization data recorded. The field was reduced to zero and then brought up once more to yield the subsequent magnetization curve. Saturation moments were obtained by constructing Honda plots from the subsequent magnetization data (Honda plots constructed from the initial magnetization data yielded saturation moments about 1 μ_B higher).

A second Faraday unit, capable of operating between 300 and 1100 K, was used to determine sample quality and Curie temperatures.

Results and Discussion

Parent Compounds

All of the parent compounds studied were single phase, cubic materials, presumably possessing the Th_6Mn_{23} structure. From the crystallographic point of view there is an interesting feature exhibited by the parent materials. There is a pronounced minimum in the lattice parameter corresponding to the composition $Er_4Y_2Fe_{23}$ (see Fig. 1).

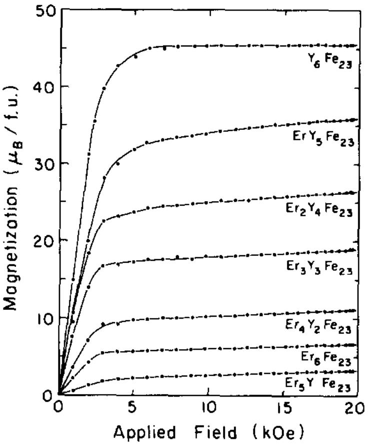

FIG. 2. Parent alloys: magnetization versus applied field at 4.2 K obtained after previous exposure to 20 kOe applied field at 4.2 K.

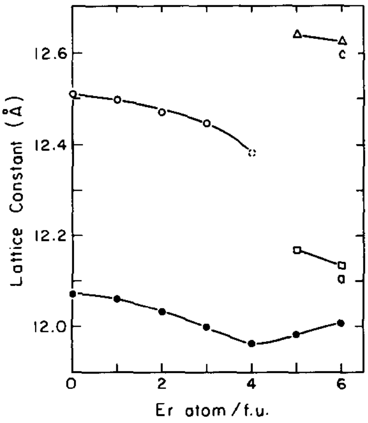

FIG. 1. Lattice parameters versus composition measured at room temperature. ○, △, □: hydrides; ●: parent alloys.

Results of the magnetic measurements are given in Figs. 2–4. In Fig. 4 the point corresponding to the composition Er_6Fe_{23} is plotted as having a negative saturation magnetization; this is because in this compound the net moment at 4.2 K points in the direction of the Er moment, whereas in the others it points in the direction of the Fe moment, as evidenced by the presence of the compensation point (Fig. 3). The line

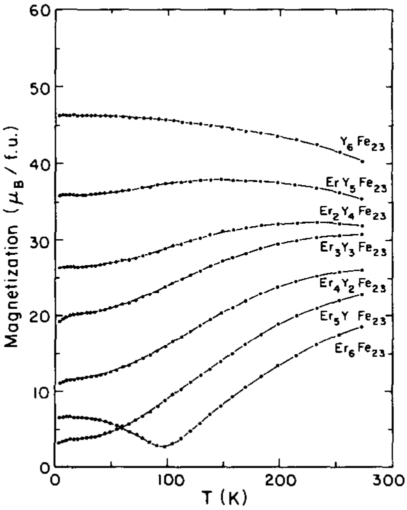

FIG. 3. Parent alloys: magnetization versus temperature in an applied field of 20 kOe.

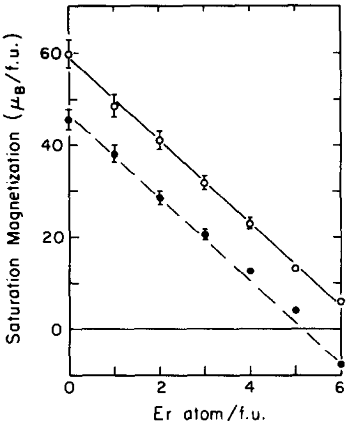

FIG. 4. Saturation magnetization versus composition: ○, hydrides; ●, parent alloys.

drawn through the points in Fig. 4 is that predicted assuming the Fe moment to be constant and the Er to contribute its full 9 μ_B free ion moment coupled antiparallel to the Fe moments. The fact that the experimental data fit the predicted line quite well confirms that the Er moment is coupled antiparallel to the Fe moment and indicates that it is not significantly quenched by crystal field effects, as is thought to be the case in Er_6Mn_{23} (*12*).

It appears that in Er_6Fe_{23} the Er and Fe moments remain constant and couple antiparallel as the sample is magnetized. The effect of the crystal field interaction is limited to conferring anisotropy on the material. In Er_6Mn_{23}, on the other hand, the crystal field rigidly binds the Er moments to the crystallographic axes and upon magnetization only the Mn moments rotate. The Er–Mn exchange is a small effect acting only to inhibit rotation of the Mn moments. Hence, the relative strengths of the *R–T* exchange and crystal field interactions are opposite in Er_6Fe_{23} and Er_6Mn_{23}.

Although the experimental data match the predicted line quite well, there are two data points, those corresponding to Er_4Y_2 Fe_{23} and Er_5YFe_{23}, which show noticeable deviation. It is worth noting that these compositions correspond to alloys possessing the smallest lattice parameters. This is an interesting correlation, but it fails to provide a basis for understanding this deviation. The two most probable causes for deviation from the theoretically predicted line are (1) slight quenching of the Er moment, and (2) Fe moment differing from that in Y_6Fe_{23}, either of which could be correlated with the lattice parameter minimum. If the deviation originates with a quenched Er moment, it could be argued that this occurs because the crystal field is maximal when the interatomic spacing is minimal. An increased Fe moment could also be related to the lattice parameter minimum through some type of band structure effect.

The Curie temperatures of the parent compounds showed little variation throughout the series, ranging from a minimum of 480 K for Y_6Fe_{23} to 503 K for Er_6Fe_{23}.

Hydrides

The hydrides studied are those which are stable at 1 atm with respect to desorption. The hydrogen content of the various hydrides is given in Fig. 5. A comparison of Figs. 1 and 5 shows a definite relationship between the parent lattice parameter and the amount of hydrogen which is retained under ambient pressure. The correlation between hydrogen content and lattice size is similar to that mentioned above between saturation magnetization and lattice size. It is impossible to say whether the variation in hydrogen content is a result of the lattice parameter variation or whether both properties represent two different manifestations of some more fundamental effect (i.e., differences in electronic structure).

The $Er_xY_{6-x}Fe_{23}$ hydrides are very interesting from a crystallographic point of view. As alluded to in the introduction, it is known from a previous investigation that the high pressure (~40 atm) hydride of Er_6Fe_{23} possesses a face-centered tetragonal structure (*10*). As previously men-

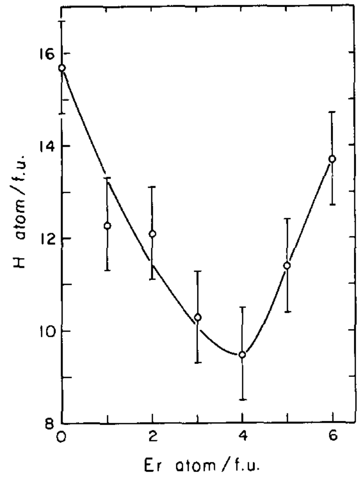

FIG. 5. Compositional dependence of hydrogen content of $Y_{6-x}Er_xFe_{23}$ alloys for an applied hydrogen pressure of 1 atm.

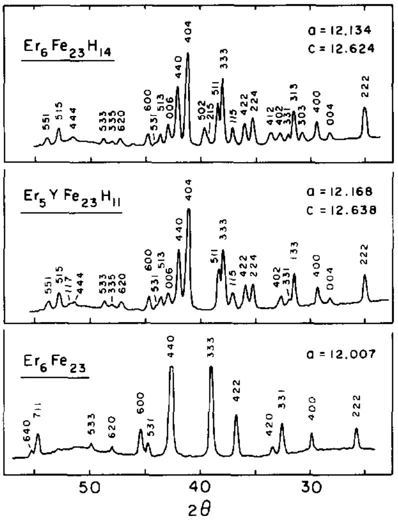

FIG. 6. X-ray powder diffraction patterns, exemplifying the various structures observed.

tioned, the current study involves the hydrides which are stable at atmospheric pressure. The lattice parameters for these hydrides are given in Fig. 1. The Y-rich (Er $\leq$ 3 atom/f.u.) hydrides are single-phase materials which retain the fcc structure of the parent compound. The hydride of $Er_4Y_2Fe_{23}$ is multiphase, the greatly predominant phase being fcc, with the lattice parameter given in Fig. 1. It is observed that for these hydrides the lattice parameter decreases monotonically with increasing Er content, as do both the lattice parameters of the parent compounds and the hydrogen content. As the Er content reaches 5 Er atom/f.u., the lattice parameter does not begin to increase, as one would a priori expect, but rather the Er-rich hydrides adopt a tetragonal crystal structure with an axial ratio of 1.03. The X-ray diffraction patterns of $Er_5YFe_{23}H_{11}$ and $Er_6Fe_{23}H_{14}$ are reproduced in Fig. 6, along with that of Er_6Fe_{23}. The indices given in the figure for the tetragonal structures are based on a nonstandard tetragonal cell, since this is the cell which best represents a distorted version of the parent compound. The structure of $Er_5YFe_{23}H_{11}$ appears to be face-centered, as is evidenced by the absence of mixed-index reflections. This face-centered structure is similar to that observed previously for the high-pressure hydride of Er_6Fe_{23}. The X-ray diffraction pattern of $Er_6Fe_{23}H_{14}$ can also be indexed with the same tetragonal cell used for $Er_5YFe_{23}H_{11}$; however, the presence of mixed-index reflections indicates that the structure is primitive, in this case, and not face-centered.

Results of the magnetic measurements are given in Figs. 7 and 8 and are summarized in Fig. 4. The line through the hydride data points in Fig. 4 is similar to that drawn through the parent data. Both the increase in saturation magnetization and the disappearance of the compensation point indicate that the Fe moment is increased by hydrogenation. The value of the Fe moments calculated for Y_6Fe_{23} and $Y_6Fe_{23}H_{16}$ are given in Table I, along with some values obtained from the literature (*13*, *14*). As is evidenced in the table, the saturation moment of both Y_6Fe_{23} and $Y_6Fe_{23}H_x$ are significantly greater than that reported by Buschow (*14*). It is also shown in the table that the saturation moment of Y_6Fe_{23} obtained

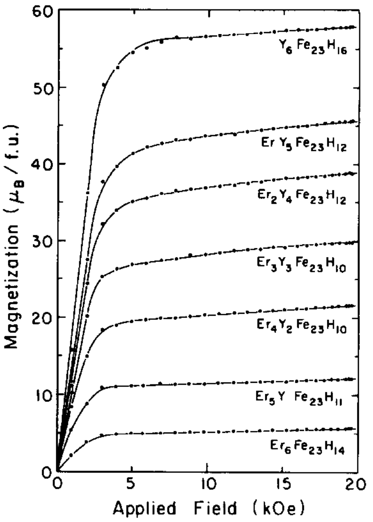

FIG. 7. Hydrides: magnetization versus applied field at 4.2 K obtained after previous exposure to 20 kOe applied field at 4.2 K.

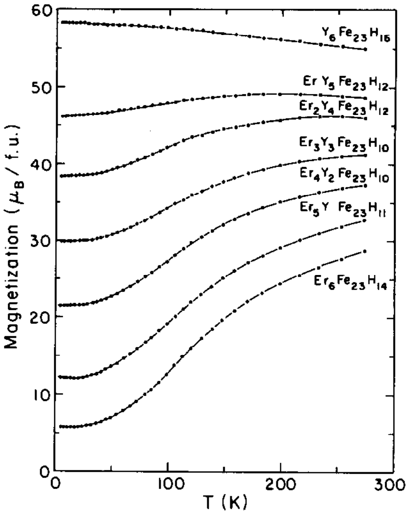

FIG. 8. Magnetization versus temperature in an applied field of 20 kOe.

in this work is in excellent agreement with that obtained previously in this laboratory by Bechman *et al.* (*13*) using a completely different technique. A possible explanation of the increase in Fe moment upon hydrogenation, in terms of electron transfer from Fe to hydrogen, has been put forth previously (*4, 15*).

It can also be inferred from Fig. 4 that the Er moment is coupled antiparallel to the Fe moment in the hydrides, as it is in the parent compounds. The magnetism of the hydrides is similar to that of the parent compounds, inasmuch as the *R–T* exchange interaction is the dominant factor in both cases. The smooth variation in magnetization with composition indicates that, for these systems at least, it is quite insensitive to structural details. Although it is evident from Fig. 4 that the Er moment is not quenched to the extent that it is in Er_6Mn_{23}, it cannot be inferred that the Er contributes exactly 9 μ_B/Er atom, as the excellent fit would seem, at first sight, to indicate. This is because, as mentioned earlier, the hydrogen content also varies with composition. This could produce a changing Fe moment.

TABLE I

SATURATION MAGNETIZATION (μ_B/Fe atom)

	Present work	Bechman *et al.*[a]	Buschow[b]
Y_6Fe_{23}	1.9 (4.2 K)	1.96 (4.2 K)	1.65 (4.2 K)
$Y_6Fe_{23}H_x$	2.59 (4.2 K)	—	1.96 (4.2 K)

[a] Ref. (*13*).
[b] Ref. (*14*).

Although it was not possible to obtain accurate Curie temperatures because of the possibility of hydrogen desorption, it was observed that hydrogen absorption invariably brought about a significant increase in the Curie temperature. In this respect the results are in agreement with those of Buschow (*14*). The observed Curie temperatures ranged between 600 and 700 K. However, as mentioned above, the Curie temperatures measured do not necessarily refer to systems possessing the original amount of hydrogen.

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