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Magnetic and Structural Characteristics of Ho_6Fe_{23} Deuterides*

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The pressure–composition isotherm of the Ho_6Fe_{23}–D_2 system at 0°C was established, revealing the presence of two plateau regions. Using the isotherm, five comopsitions of the Ho_6Fe_{23}–D_x system (x = 0, 1.5, 8.2, 12.1, 15.7) were selected for investigation. These were examined by X-ray diffraction and magnetization measurements. The cubic lattice of the host metal is maintained to $x = 8.2$. A tetragonal structure develops at $x = 12.1$, but this reverts to cubic symmetry at the highest deuterium concentration studied. The observed structural changes are ascribed to preferential site occupancies by deuterium. Absorption of 15.7 deuterium atoms per formula unit in Ho_6Fe_{23} caused a 10.2% increase of the unit cell volume. Increase in the deuterium content resulted in a striking increase in the Curie temperature T_c and in a linear decrease in compensation temperature T_{comp}. The saturation magnetization changed smoothly as the system changed from one structure type to another. There appears to be a significant increase in Fe magnetic moment upon deuterium absorption, which is ascribed to the removal of electrons from the 3*d* iron band by deuterium.

1. Introduction

Rare earth–3*d* intermetallic compounds of 6 : 23 stoichiometry show very interesting and complicated magnetic properties (*1–10*). Generally they show also a remarkable ability to absorb large amounts of hydrogen or deuterium (*5–10*). In cases when both partner atoms possess the magnetic moments, hydrogen absorption not only affects the interactions between 3*d* moments and between 4*f* moments but also between 3*d* and 4*f* moments. This leads to rather complex changes in magnetic and structural characteristics of 6 : 23 compounds.

Absorbed hydrogen or deuterium atoms are located in various interstitial sites (*6–9*) in the Th_6Mn_{23}-type (*11*) crystal structure. Since there are more sites than H or D to fill them, this leads to some atomic disorder and to a distribution of coupling strengths (assuming a band model) for each of the three coupling types, i.e., *R–R*, *T–T*, and *R–T*, where *T* represents Mn or Fe. This usually results in a significant change of the magnetic and the structural nature as compared to the parent compounds.

Ho_6Fe_{23} crystallizes in the complex fcc structure (Th_6Mn_{23}-type, space group *Fm*3*m*) with 116 atoms per unit cell (*11*). There are four inequivalent Fe crystal sites (4*b*, 24*d*, 32f_1, 32f_2) and a unique (24*e*) rare earth site. Neutron diffraction studies of Ho_6Fe_{23} (*12*) revealed that Fe moments are ferromagnetically coupled with each other, and antiferromagnetically coupled with the

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Ho moment. The influence of hydrogenation on the properties of Ho_6Fe_{23} has not been studied thoroughly to date. Only one composition ($Ho_6Fe_{23}H_{16}$) has been investigated (7). This showed upon hydrogenation an increase of the average Fe moment and a 9% increase of the cubic unit cell. A change in the compensation temperature was also reported.

In this study we present the pressure-composition isotherm for the Ho_6Fe_{23}–D_2 system at 0°C and the results of X-ray and magnetic measurements of selected deuterides of that system. A remarkable change in magnetic behavior is observed as well as a change in crystal structure.

2. Experimental Details

Samples were prepared from metals of 99.9% purity (Ho—Research Chemicals; Fe—Atomergic Chemetals Corp.). Stoichiometric amounts of these elements were melted several times in a water-cooled copper boat by an induction furnace. To obtain more homogeneous single phase ingots, heat treatments at 1190°C for 1 to 2 weeks were performed.

Initially a pressure-composition isotherm (PCI) at 0°C was established to determine the composition range of the single phase regions. Samples of approximately 15 g were used. A stainless steel sample chamber and manifold, together with a Bourdon type gauge, were utilized in procurring the above-atmospheric PCI. To determine subsequent lower equilibrium pressure points, 100 ml or less increments of D_2 were removed via the displacement of water in an inverted buret. The below-atmospheric isotherm was measured using a glass system in which a Toepler pump removed increments of D_2. The pressure was read from a Hg manometer by a cathetometer (±0.05 Torr). The amount of time needed for the equilibrium pressure to be reached ranged from 1 to 5 hr. The equilibrium points were calculated using the Beattie–Bridgeman equation of state.

For samples of composition $Ho_6Fe_{23}D_x$, $x = 8.2$, 12.1, 15.7, deuterium was removed (sample at 0°C; initially $x \approx 18$) until the desired composition was obtained. The deuterides were allowed to equilibrate overnight and then were poisoned with SO_2 to prevent escape of D_2. For $Ho_6Fe_{23}D_{1.5}$, the sample preparation was similar, the difference being a sample temperature of 300°C and an avoidance of SO_2 poisoning. X-ray diffraction patterns indicated no decomposition of the parent material and homogeneous deuterides for all the loaded samples.

Magnetic measurements were performed by use of the Faraday technique in the temperature range 4.2 to 1000 K and in applied fields up to 20 kOe. The accuracy in the experimental measurements is about ±4%.

3. Results and Discussion

The pressure-composition isotherm for the Ho_6Fe_{23}–D_2 system determined at 0°C is shown in Fig. 1. It reveals the existence of at least two (narrow) plateau regions ($\alpha + \beta$ and $\beta + \gamma$ phases). Sample compositions of $Ho_6Fe_{23}D_x$, $x = 8.2$, 12.1, and 15.7, were selected from one phase (or approximately one phase) regions according to that isotherm. The sample of composition $x = 1.5$ was chosen from the hypothesis that the most stable deuterium state is the rare earth octahedral site. Deuterium occupation of that site would yield a composition $Ho_6Fe_{23}D_1$. Using as a rough approximation the free energy of hydride formation of the rare earth dihydride, a deuterium partial pressure of the order $<10^{-32}$ atm at 300°C would be needed to remove deuterium from the octahedral sites. Therefore the $Ho_6Fe_{23}D_{1.5}$ is considered to be also in a single phase region.

X-ray diffraction data for the parent material Ho_6Fe_{23} and the deuterides (see Table

TABLE I

CRYSTALLOGRAPHIC AND MAGNETIC DATA OBTAINED FOR Ho_6Fe_{23} AND SELECTED DEUTERIDES

Material	a (Å)	c (Å)	$\frac{\Delta V}{V} \cdot 100\%$	T_c (K)	T_{comp} (K)	M_{sat} (μ_B/f.u.)
Ho_6Fe_{23}	12.049	—	0.00	510	185	16.5
$Ho_6Fe_{23}D_{1.5}$	12.050	—	0.03	575	170	15.9
$Ho_6Fe_{23}D_{8.2}$	12.242	—	4.81	671	120	14.6
$Ho_6Fe_{23}D_{12.1}$	12.209	12.577	7.10	696	98	11.4
$Ho_6Fe_{23}D_{15.7}$	12.445	—	10.22	702	72	7.2

T_c error: ±6 K
T_{comp} error: ±4 K
M_{sat} error: ±0.3 μ_B/f.u.

I and Fig. 2) show an increase of the unit cell volume upon deuteration. Low concentration of deuterium has very little influence on the lattice parameter and does not affect the crystal structure type. It seems reasonable to conclude that initially deuterium enters into spacious octahedral interstitial sites formed by the Ho atoms. For the crystallographically similar system, $Y_6Mn_{23}D_x$, it has been established that this is the case. Conversely, $Th_6Mn_{23}D_x$ (for which Th is in the 4^+ state) does not have deuterium occupancy of the octahedral site (*6*). After the octahedral sites are filled (assuming the $Y_6Mn_{23}D_x$ model), deuterium next occupies the higher energy sites (tetrahedral) and distorts the lattice in one specific direction, causing a structure transformation from cubic to tetragonal. The sample $x = 12.1$ shows a tetragonal crystal structure with a rather small (3%) preferential change of the lattice parameter. When more deuterium is pushed into the tetragonal unit cell another preferential distortion occurs (this time along the tetragonal a axis) and the cubic crystal structure is reestablished in the γ phase. The sample with $x = 15.7$ shows the cubic structure again. The $Ho_6Fe_{23}D_{12.1}$ X-ray diffraction pattern indexed perfectly to a tetragonal structure. The 222 peak is not split, confirming that this hydride is *not* a mixture of two cubic phases. The diffraction pattern of the $x = 12.1$ sample is exactly of the same type as that published in Ref. (16) for $Er_6Fe_{23}H_{14}$.

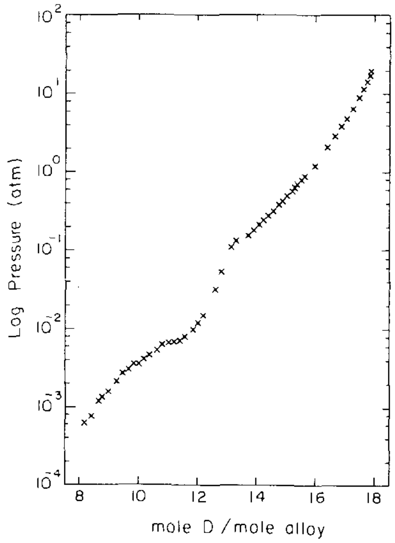

FIG. 1. Pressure–composition isotherm for the Ho_6Fe_{23}–D_2 system at 0°C.

The crystal structure changes mentioned above as well as the presence of deuterium in the material cause significant changes in its magnetic behavior. The magnetization data obtained are summarized in Table I and are shown in Figs. 2–5. The peaks in $M(T)$ taken at 4 kOe (Fig. 4) suggest intrin-

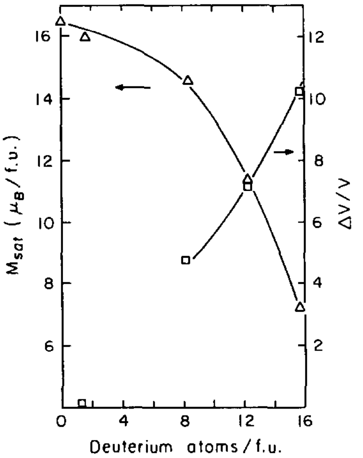

FIG. 2. Plot showing the change of the unit cell volume (at room temperautre) $\Delta V/V$ and saturation magnetization (4.2 K), M_{sat}, as a function of the deuterium absorbed by Ho_6Fe_{23}.

sic hardness as a result of the atomic disorder. The $M(T)$ curves measured at an applied field of 20 kOe do not show such peaks. Saturation magnetization at 4.2 K, M_{sat}, was obtained from $M(1/H)$ plots by extrapolation to $H = \infty$. It can be noticed that low concentrations of deuterium have little influence on M_{sat} but have significant effect on the Curie temperature T_c even though the distances in the lattice are not changed significantly. On the other hand, for high deuterium concentration T_c does not change significantly while the saturation moment drops dramatically. On the basis of the localized model, both facts suggest that Fe–Fe interactions that have the strongest influence on T_c are very much changed by deuterium. Probably deuterium in tetrahedral sites (higher deuterium compositions) has also a strong effect on Ho–Fe interactions, which results in a small change of T_c. In the octahedral sites deuterium may influence Ho–Ho interactions, but due to the fact that Fe–Fe interactions are the strongest, one does not observe drastic changes in M_{sat}.

The localized picture involved in the above discussion may not be appropriate here, and a band model should perhaps be applied to explain the magnetic behavior of the $Ho_6Fe_{23}D_x$ system. However, band structure calculations for such complicated systems are not available. The saturation moment seems to change smoothly from one structure type to another (cubic to tetragonal and vice versa). The reason for

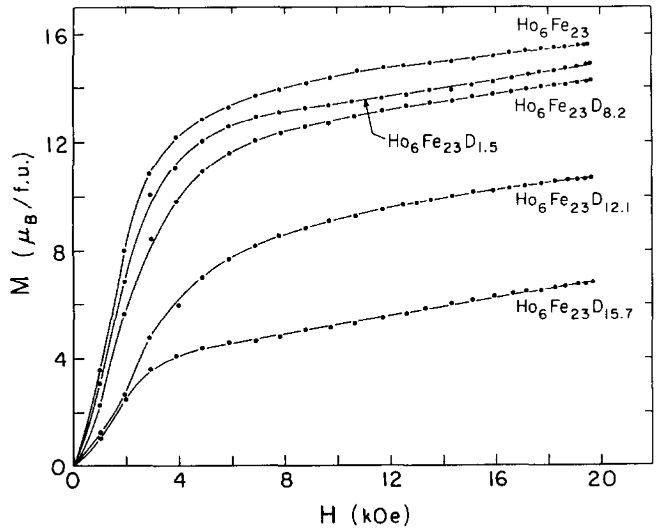

FIG. 3. Dependence of magnetization on an applied field at $T = 4.2$ K for Ho_6Fe_{23} and its deuterides.

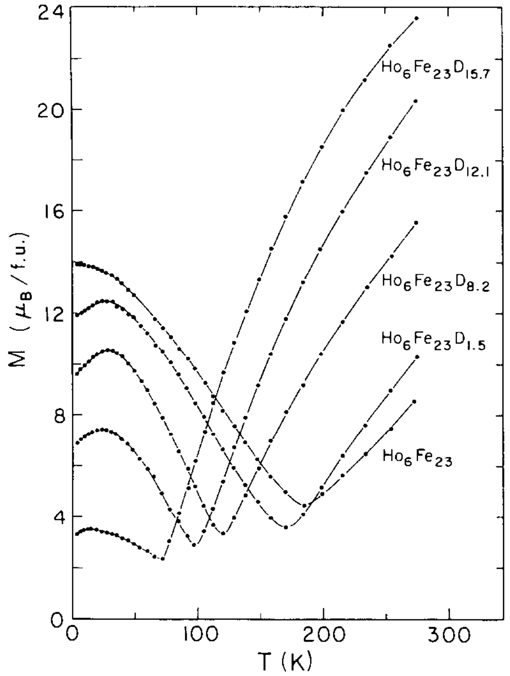

FIG. 4. Temperature dependence of magnetization in an applied field of 4 kOe for Ho_6Fe_{23} and selected deuterides.

that may be that the interatomic distances for the magnetic ions in the two structures are nearly the same, and hence exchange is about the same.

Some doubt may be involved in reporting and discussing the Curie temperatures of deuterides because already at 530 K the SO_2 poisoning for all the poisoned samples seemed to stop being effective. Small kinks on $M(T)$ curves, attributed to the SO_2 release, were observed for all poisoned samples at 530 K. The kink at 530 K was not observed for the $x = 1.5$ sample which was not poisoned. If desorption of deuterium did occur during the high temperature M vs T measurements, then some irregularities would appear in the shape of the magnetic curves. Also, some anomalies would be observed from sample to sample. This was not the case in our measurements. Conversely, very sharp drops of magnetization were observed at T_c, and the change in T_c from sample to sample was continuous. This gives some credibility to the T_c data. The decomposition of all samples was observed at the temperature of about 960 K.

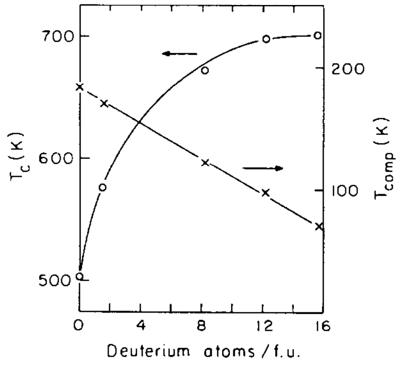

FIG. 5. Variation of the Curie temperature (T_c) and compensation temperature (T_{comp}) as a function of the deuterium absorbed by Ho_6Fe_{23}.

The compensation temperature was determined from low field (4 kOe) curves and shows a linear drop with the increase of the amount of deuterium absorbed by Ho_6Fe_{23}. It is worth noting that at low temperatures the Ho net magnetization is dominant, while the Fe magnetization dominates at higher temperatures. The decrease in magnetization (last column, Table I) can be ascribed to (1) a diminished Ho moment, (2) an increase in the moment of Fe, or (3) a combination of these. If it is ascribed to (2), the Fe moment is increased by hydrogenation by ~0.4 μ_B per atom. This is the increment in Fe moment observed between Y_6Fe_{23} and $Y_6Fe_{23}H_{16}$, making it appear that hydrogenation affects primarily the Fe moment. This is rather common in the hydrogenation of rare earth–iron compounds (*13, 14*). Elsewhere, one of us (WEW) has described this in detail and attributed the increase to a removal of electrons from the iron *d* band and transfer into lower-lying hydrogen–metal bonding states (*15*).

Further details concerning the distribution of deuterium as well as the distribution of magnetic moments in sublattices of the $Ho_6Fe_{23}D_x$ system may be obtained from neutron diffraction measurements. These measurements are currently in progress.

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