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Letter

Forced-ferromagnetic state in a Tm₂Fe₁₇H₅ single crystal

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Abstract

We report the attainment of the ferromagnetic state in an interstitially modified heavy rare-earth-iron intermetallic compound in an external magnetic field. The starting composition is RE₂Fe₁₇, which is the RE–Fe binary richest in iron. We concentrate on the Tm–Fe compound, which is the most sensitive to magnetic field. The maximum possible amount of hydrogen (5 at.H/f.u.) is inserted into a Tm₂Fe₁₇ single crystal. We demonstrate that in a magnetic field of 57 T Tm₂Fe₁₇H₅ reaches the ferromagnetic state with an enviably high polarization of 2.25 T.

Keywords: single crystal, hydride, forced-ferromagnetic state, rare-earth-iron intermetallic compound

(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetism of the rare-earth (RE)—iron intermetallic compounds is of special importance in view of applications. Suffice it to mention the celebrated Nd₂Fe₁₄B magnet, in which light boron stabilizes the crystal structure. The Sm₂Fe₁₇N_{*x*} system, interstitially modified with nitrogen (here *x* ranges between 2 and 3), has some advantages over Nd₂Fe₁₄B due to its high fundamental characteristics (such as magnetic polarization, Curie temperature, anisotropy constant [1, 2]), but its potential has not been realized yet [3]. Improved characteristics can rationally be reached only with a better understanding of the magnetic properties of such interstitially modified RE₂Fe₁₇ materials and for that the use of bulk, nondecrepitated single crystals is highly desirable [4].

The RE and Fe sublattices are ordered ferro- or ferrimagnetically depending on the rare-earth atom [5–11]. The total magnetic moment of light rare earths (LRE) is usually small (~3 μ_B/atom for Nd, ~0.7 μ_B/atom for Sm) and is parallel to the total magnetic moment of the iron, which results in a moderate enhancement of the net polarization. It is for this reason that LRE-Fe intermetallics are used as magnetic materials [3, 6, 12–14]. The situation in heavy rare earth (HRE)-Fe compounds is different. The total magnetic moment of HREs is as large as 10 μ_B/atom (for Dy or Ho). Unfortunately, the large total moment is of no immediate benefit, since it is antiparallel to the moment of the iron sublattice. From a fundamental point of view, the magnetic behavior of HRE-Fe compounds (ferrimagnets) is more diverse than that of ferromagnets. While a ferromagnet simply saturates in external magnetic

field, a ferrimagnet demonstrates a significant growth of mag-netization. It goes through a sequence of spin-reorientation phase transitions until it reaches the field-induced ferromagn-etic state.

Sufficiently high external magnetic fields have to be employed in order to observe a complete magnetization process along different crystallographic directions of the sample. Mutual orientation of the RE spin and orbital moments is gov-erned by the spin-orbit coupling, $H_{so} = \lambda \mathbf{S}_{RE} \cdot \mathbf{L}_{RE}$, where the coupling constant λ is largely an atomic property [15]. All HRE have λ negative and large, $|\lambda| \sim 10^3$ K. As against that, the RE-Fe exchange interaction, $H_{ex} = J_{RE-Fe} \mathbf{S}_{RE} \cdot \mathbf{S}_{Fe}$, is two orders of magnitude weaker, $J_{RE-Fe} \sim 10$ K [16]. In a favorable case, a magnetic field of several dozen Tesla should suffice to align \mathbf{S}_{RE} and \mathbf{S}_{Fe} parallel. More importantly, J_{RE-Fe} is not an atomic constant. It varies from compound to com-pound, depending in particular on interatomic distances [6].

Here, we report the attainment of the ferromagnetic state in HRE-Fe single-crystalline hydrides, observed in high magn-etic fields. It is advantageous to perform such experiments on Tm-Fe compounds. Since thulium is the HRE with a Landé factor closest to unity, it takes the smallest applied magnetic field to reach the ferromagnetic state (for a given J_{RE-Fe}). For the same reason, the field in our experiments was always applied along the easy magnetization direction of single-crystalline samples.

Earlier, a $\text{Tm}_2\text{Fe}_{17}$ single crystal and its polycrystalline deuteride $\text{Tm}_2\text{Fe}_{17}\text{D}_{3.2}$ were studied in fields up to 74 and 60 T, respectively [17]. Unfortunately, Isnard *et al* did not reach the ferromagnetic state in both compounds. In the present work, samples with various hydrogen content, including the maximum possible amount of 5 at.H/f.u., were used. We showed that $\text{Tm}_2\text{Fe}_{17}\text{H}_5$ reaches the ferromagnetic state in a magnetic field of 57 T and attains an enviably high polarization of 2.25 T. The study is performed on single-crystalline $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ samples that allowed us to obtain reliable data on the type and behavior of the magnetocrystalline anisotropy in these materials.

2. Materials synthesis and experimental details

Initial samples were prepared by arc-melting of 99.9% pure elements under helium atmosphere. To stimulate growth of single-crystalline grains, the ingots were re-melted and cooled down slowly in a resistance furnace. Several 1 mm-large grains were extracted and checked by x-ray Laue technique. Usually single crystals decrepitate when exposed to hydrogen. To prevent this from happening, the hydrogenation was carried out under particularly mild conditions—elevated temperature and low partial pressure of H_2 —both of which slow down the reaction. The higher hydrogen contents were achieved by subsequently raising the pressure. The amount of absorbed hydrogen in $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ was determined from the pressure drop in the reaction chamber. Phase composition of the samples was controlled by powder x-ray diffraction. Magnetization measurements were performed by using a pulsed-field induction magnetometer [18] at the Dresden High

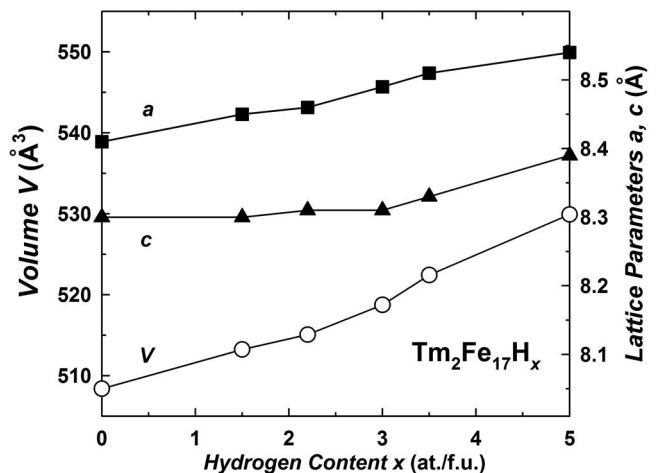


Figure 1. The lattice parameters a and c and the unit cell volume V of $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ (lines are guides to the eye).

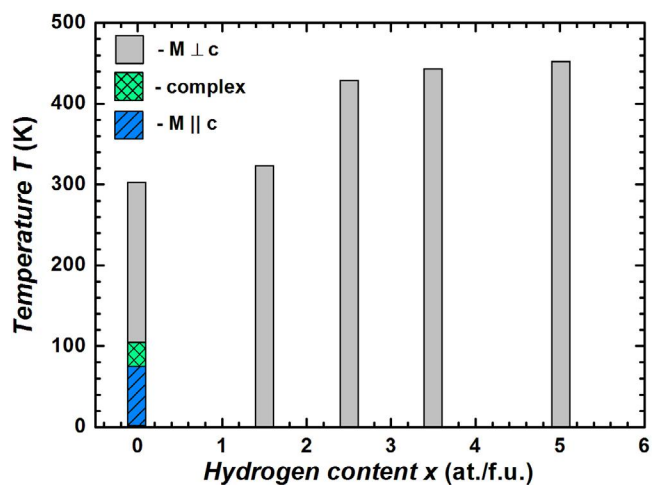


Figure 2. Magnetic phase diagram demonstrating the orientation of the magnetic moment with respect to the crystal axis c for $\text{Tm}_2\text{Fe}_{17}$ and some hydrides $\text{Tm}_2\text{Fe}_{17}\text{H}_x$. The width of the bars corresponds to the experimental error in x .

Magnetic Field Laboratory. The maximum field was 60 T with a total pulse duration of 25 ms [19]. A commercial magnetometer (Quantum Design PPMS-14) was used for magnetization measurements in steady magnetic fields up to 14 T at temperatures between 2 and 500 K.

3. Results and discussion

Pure $\text{Tm}_2\text{Fe}_{17}$ has the hexagonal $\text{Th}_2\text{Ni}_{17}$ -type crystal structure (space group $P63/mmc$) with lattice parameters $a = 8.409(3)$ Å and $c = 8.300(3)$ Å. Hydrogenation increases the unit-cell volume of $\text{Tm}_2\text{Fe}_{17}$ without changing its crystal structure. The lattice parameter a of $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ grows linearly with hydrogen content x , see figure 1. However, c remains practically constant as hydrogen fills the octahedral interstitial sites (at $x < 3$), and increases in the interval $3 < x < 5$, as the tetrahedral sites are filled [20]. For the composition $\text{Tm}_2\text{Fe}_{17}\text{H}_5$, the lattice parameters are $a = 8.540(3)$ Å and $c = 8.381(3)$ Å; the relative volume change upon hydrogenation V/V is $\sim 4.2\%$.

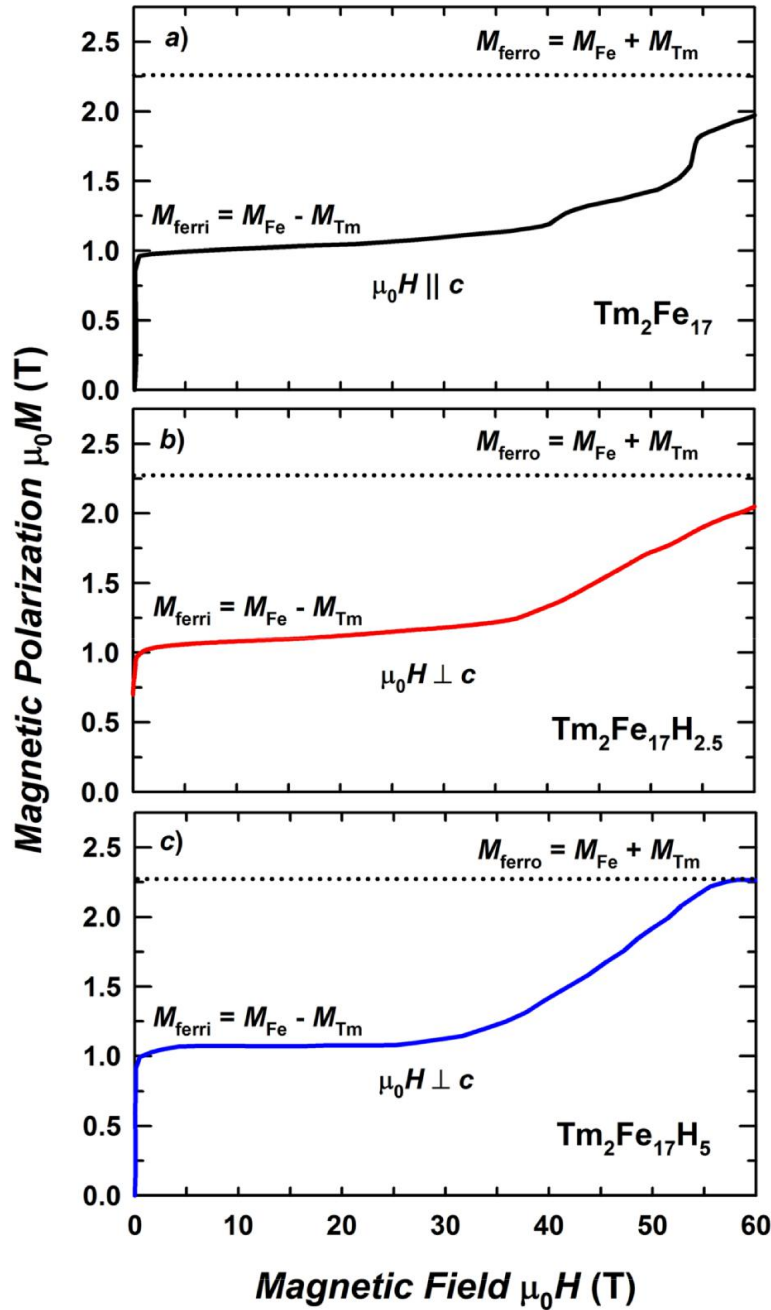


Figure 3. Magnetization curves of $\text{Tm}_2\text{Fe}_{17}$, $\text{Tm}_2\text{Fe}_{17}\text{H}_{2.5}$ and $\text{Tm}_2\text{Fe}_{17}\text{H}_5$ measured at $T = 4.2$ K in pulsed fields applied along the easy axes.

$\text{Tm}_2\text{Fe}_{17}$ is a ferrimagnet with a Curie temperature of $T_C = 295$ K and a spontaneous moment of $22 \mu_B/\text{f.u.}$

($\mu_0 M_{\text{ferri}} = 1.0$ T) at $T = 4.2$ K. Figure 2 shows the magnetic phase diagram of $\text{Tm}_2\text{Fe}_{17}$, as well as of its hydrides

$\text{Tm}_2\text{Fe}_{17}\text{H}_x$, deduced from magnetization data measured on single crystals along different crystallographic directions in a wide temperature range up to 500 K (not shown here). At low temperatures, the anisotropy of pure $\text{Tm}_2\text{Fe}_{17}$ is of the ‘easy-axis’ type; this changes to ‘easy plane’ as temperature increases. The change proceeds via an intermediate ‘easy-cone’ phase. Our results agree well with data presented in [17].

Hydrogenation is known [4] to affect strongly (i) the type of magnetic anisotropy (all investigated $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ hydrides are easy-plane magnets), and (ii) the Curie temperature (seen to rise from 295 to 450 K as x grows from 0 to 5). It also modifies significantly the magnetization curves of $\text{Tm}_2\text{Fe}_{17}\text{H}_x$, see figure 3. Here, the field was applied along the easy magnetization direction, namely, along the c axis for $\text{Tm}_2\text{Fe}_{17}$ (figure 2(a)) and perpendicular to the c axis for $\text{Tm}_2\text{Fe}_{17}\text{H}_{2.5}$ (figure 2(b)) and $\text{Tm}_2\text{Fe}_{17}\text{H}_5$ (figure 2(c)) (the basal-plane magnetocrystalline anisotropy of the studied compounds is close to zero). For $\text{Tm}_2\text{Fe}_{17}$, one can observe two rather sharp field-induced transitions, where the magnetization increases

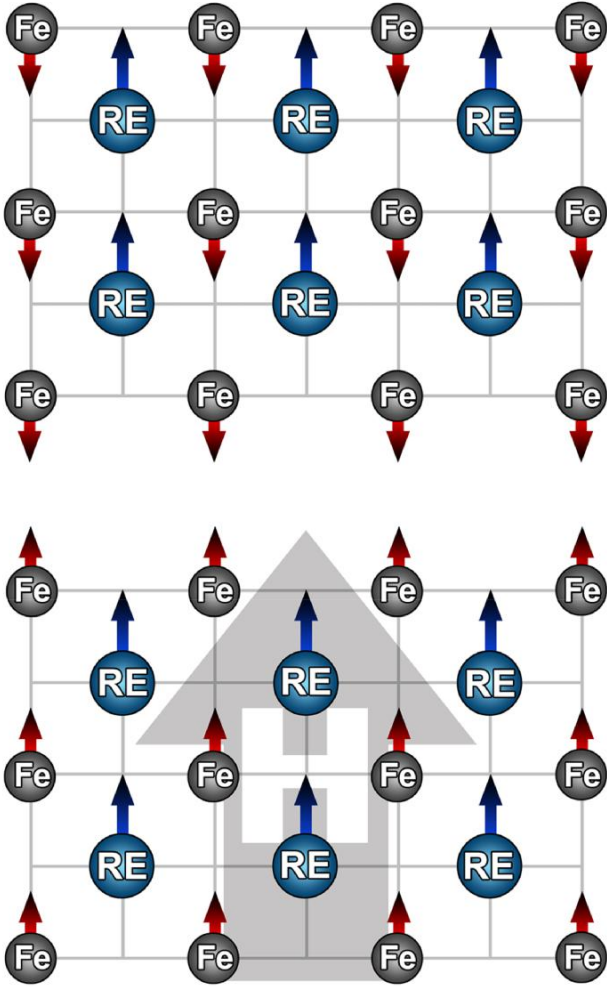


Figure 4. Ferrimagnetic (top) and field-induced ferromagnetic (bottom) states of an HRE-Fe compound.

abruptly. As against that, the magnetization of $\text{Tm}_2\text{Fe}_{17}\text{H}_{2.5}$ and $\text{Tm}_2\text{Fe}_{17}\text{H}_5$ shows a continuous growth above a certain threshold field. For the final composition with $x = 5$ the magnetic field of 57 T was sufficient for attaining the ferromagnetic state (figure 3(c)).

Let us assume for the ground state of $\text{Tm}_2\text{Fe}_{17}$ an antiparallel configuration of the Tm and Fe moments ($M_{\text{ferri}} = M_{\text{Fe}} - M_{\text{Tm}} = 22 \mu\text{B}/\text{f.u.}$) and adopt the free-ion value for the magnetic moment of Tm, $M_{\text{Tm}} = 14 \mu\text{B}/\text{f.u.}$ This yields for the iron-sublattice moment $M_{\text{Fe}} = 36 \mu\text{B}/\text{f.u.}$, which is in good agreement with what is known for $\text{RE}_2\text{Fe}_{17}$ [13]. In the forced ferromagnetic state, $\text{Tm}_2\text{Fe}_{17}$ should have $M_{\text{ferro}} = M_{\text{Fe}} + M_{\text{Tm}} = 50 \mu\text{B}/\text{f.u.}$ ($\mu_0 M_{\text{ferro}} = 2.29 \text{ T}$). For $\text{Tm}_2\text{Fe}_{17}\text{H}_5$, $M_{\text{ferri}} = 23 \mu\text{B}/\text{f.u.}$ and $M_{\text{ferro}} = 51 \mu\text{B}/\text{f.u.}$, that is, $\mu_0 M_{\text{ferri}} = 1.02 \text{ T}$ and $\mu_0 M_{\text{ferro}} = 2.25 \text{ T}$. In both compounds, the magnetization more than doubles as a result of the ferri-to-ferro transition. Since hydrogenation weakens the Tm-Fe exchange we are able to observe the ferromagnetic state for $\text{Tm}_2\text{Fe}_{17}\text{H}_5$ already at 57 T (figures 3(c) and 4). Neglecting the weak Tm-Tm interaction, one can consider the Tm-Fe exchange integral J_{TmFe} to be proportional to the molecular

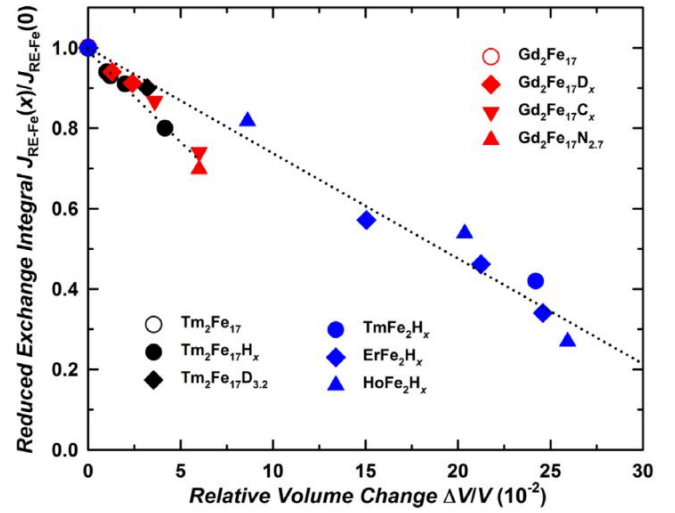


Figure 5. Reduced exchange integral $J_{\text{RE-Fe}(x)}/J_{\text{RE-Fe}(0)}$ for $\text{RE}_2\text{Fe}_{17}(\text{H, N, C})_x$ (RE = Gd [22, 23], Tm) and REFe_2H_x (RE = Ho, Er, Tm [25–27]) as a function of the relative volume change V/V .

field on Tm. The latter can be determined by several methods [16, 6, 17] In [17], it was shown that the molecular field is just given by the abscissa of the midpoint of the sloping part of the experimental magnetization curve. Since the proportionality coefficient is not accurately known, it is convenient to describe the effect of hydrogen on J_{TmFe} by means of the reduced quantity, $J_{\text{TmFe}(x)}/J_{\text{TmFe}(0)}$, i.e. the exchange integral or the molecular field normalized to unity for the parent compound. This is plotted for $\text{Tm}_2\text{Fe}_{17}\text{H}_x$ versus the relative volume change, V/V , as determined from the lattice parameters (figure 5). In agreement with earlier observations [21], $J_{\text{RE-Fe}(x)}/J_{\text{RE-Fe}(0)}$ decreases as a result of hydrogenation. Moreover, in figure 5 we present similar data for $\text{Gd}_2\text{Fe}_{17}(\text{D, N, C})_x$ compounds, whose molecular fields were determined by use of inelastic neutron scattering [22, 23]. All data can be approximated by a straight line.

Interestingly, the $J_{\text{RE-Fe}}$ data plotted against relative volume change in $\text{HREFe}_2\text{-H}$ systems (figure 5) also demonstrate a linear trend for the HRE Ho, Er and Tm [24–26]. Hydrogenation of the cubic Laves phases REFe_2 can well produce values of V/V between 25 and 30%, while in $\text{RE}_2\text{Fe}_{17}$ by way of hydrogenation, nitrogenation, and/or carbonation a volume increase of just under 9–10% appears [1]. For REFe_2 , the exchange fields weaken by up to about 70%, whereas for $\text{RE}_2\text{Fe}_{17}$, it weakens by 20–30%. Despite the considerable decrease of J_{TmFe} , high magnetic fields are required in order to attain the forced-ferromagnetic state in TmFe_2H_x due to the increased magnetocrystalline anisotropy upon hydrogenation caused by the structural phase transition from the parent cubic to the rhombohedral structure.

4. Conclusions

The study of the field-induced transitions from a ferri- to a ferromagnetic state in the intermetallic compounds is an interesting fundamental problem. Up to now very few forced-ferromagnetic states in rare-earth intermetallic compounds

with iron were reported [24, 27]. In the present work, the measurements were carried out on single-crystalline Tm₂Fe₁₇ hydrogenated to the maximum hydrogen content of 5 H atoms per formula unit along the easy magnetization direction in fields up to 60 T. Hydrogenation allowed us to decrease the Tm–Fe exchange and thus to lower the transition field to the forced-ferromagnetic state down to 57 T as compared to about 80 T expected for the parent compound Tm₂Fe₁₇ [17]. In the ferromagnetic state, Tm₂Fe₁₇H₅ attained an enviably high polarization of 2.25 T. The larger value $\mu_0 M_{\text{ferro}} = 2.65$

T can be obtained for Ho₂Fe₁₇ in the even higher applied magnetic field (84 T [18]). (Other numbers for comparison: the celebrated hard magnetic material Nd₂Fe₁₄B has 1.85 T at T = 0 K while this value in the industrial magnets does not surpass 1.5 T).

Although it may take a lower magnetic field to stabilize ferromagnetism in Co-based compounds, e.g. 39 T sufficed for Tm₂Co₁₇ [28], polarization in the ferromagnetic state is lower, too ($\mu_0 M_{\text{ferro}} = 1.96$ T for Tm₂Co₁₇). The search for new multicomponent compounds with substitutional or/and interstitial atoms where a transition into a high-magnetization state takes place at even lower magnetic field is of practical importance. Further progress in this field can be anticipated.

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